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AMERICAN LEATHER CHEMISTS ASSOCIATION

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CONTENTS:

Bureau of Employment - - - - - - - - - - - - - - - 117

The Correlation Between Some Physical Properties of Leather *By* WILLIAM T. RODDY and ROBERT M. LOLLAR 118

The Chemistry of Vegetable Tannins. VI Physical Data *By* ROBERT C. PUTNAM - - - - - - - - - 125

Acetyl Determination Methods for Substituted Black Wattle Tannins *By* D. G. ROUX - - - - - - 133

The Effect of Microbiological and Pancreatic Bates on Limed Skins *By* RAYMOND ELING and ROBERT M. LOLLAR - - - - - - - - - - - - - - - - - 135

Amide Nitrogen of Collagen and Hide Powder *By* JAMES M. CASSEL and ELIZABETH MCKENNA - - - - - - 142

The Over-All Basicity of Chrome Tanned Leather *By* R. L. STUBBINGS and EDWIN R. THEIS - - - - - - - 155

Book Notice - - - - - - - - - - - - - - - - - - 168

Abstracts - - - - - - - - - - - - - - - - - - - 169

Patents - 181

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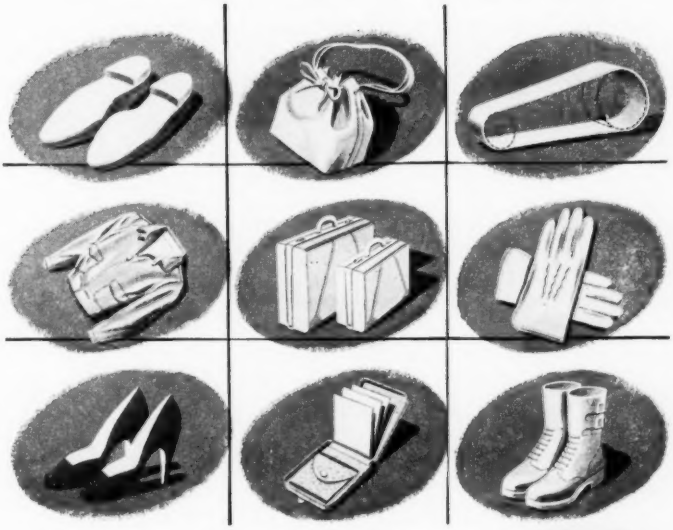

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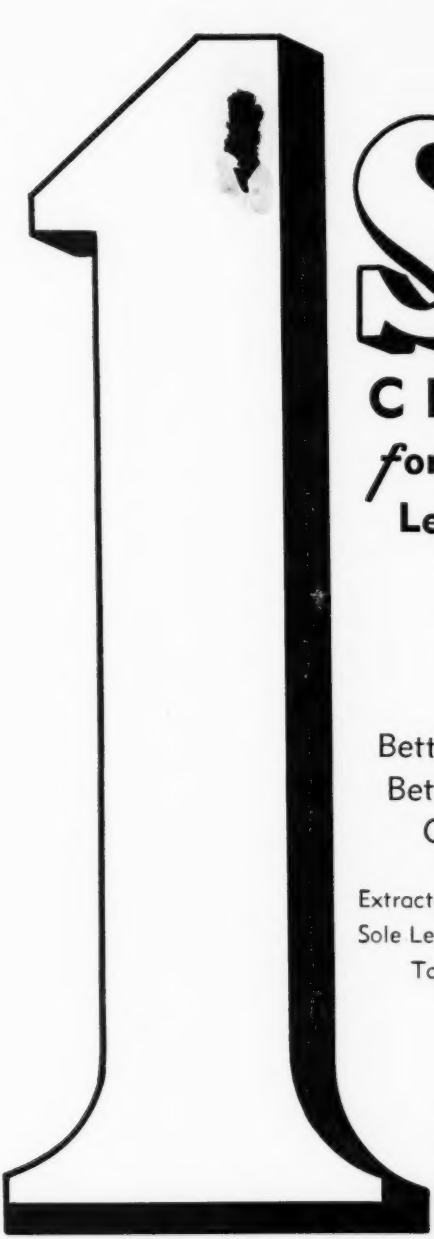

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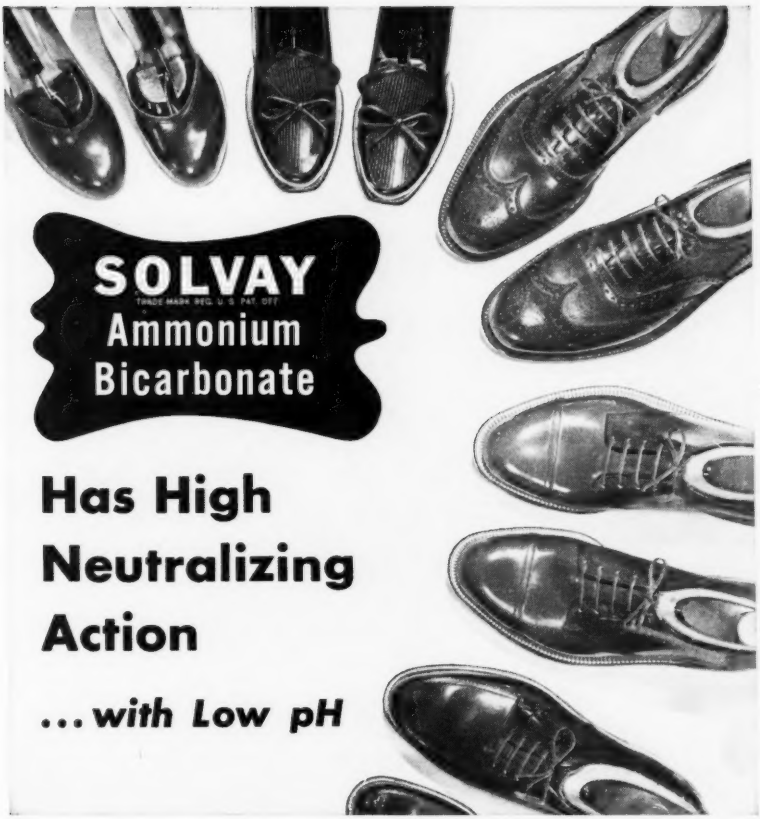

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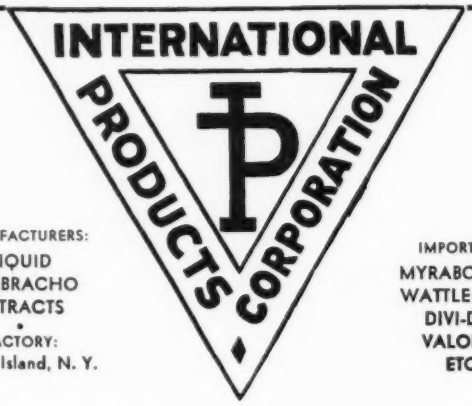

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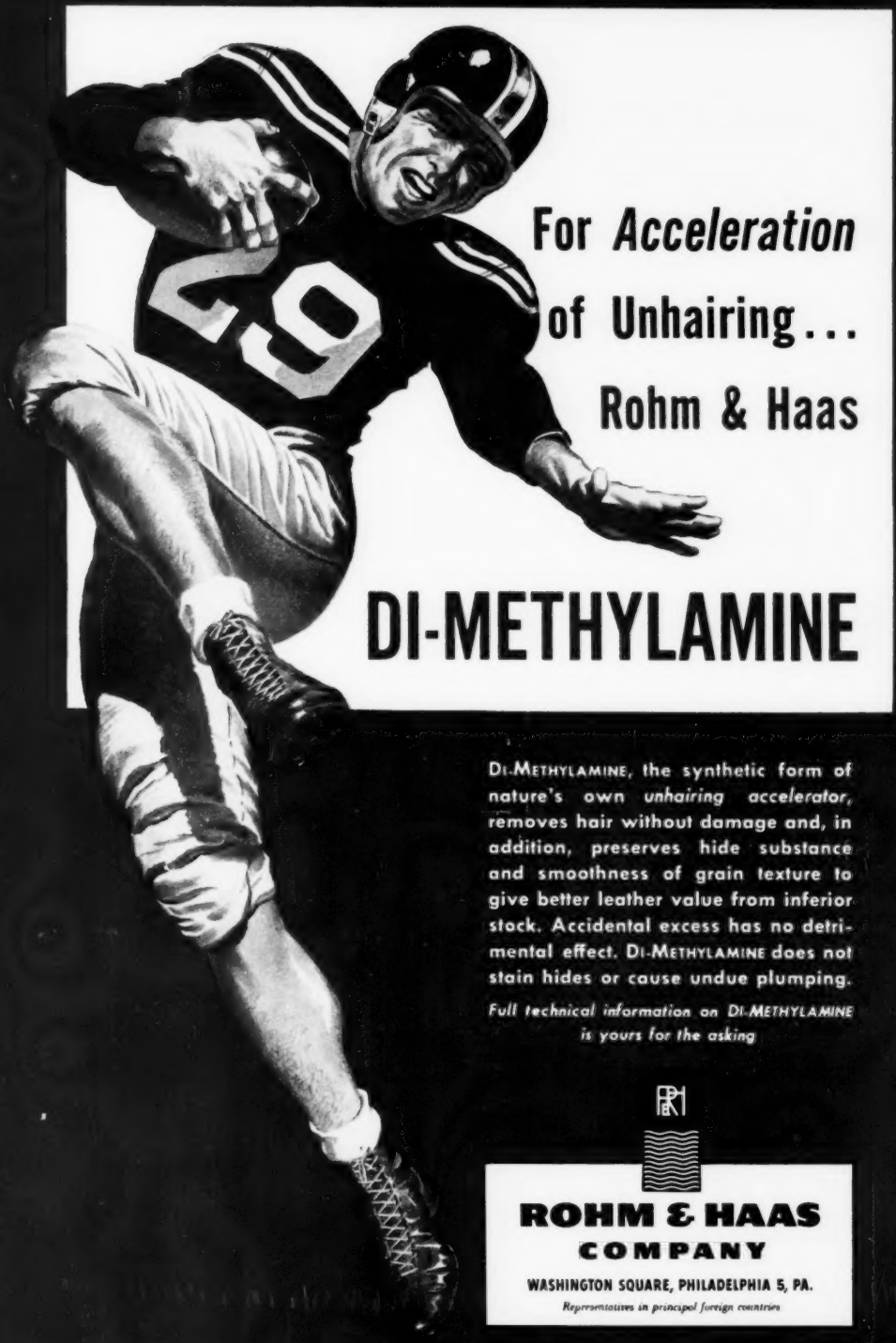

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The Correlation Between Some Physical Properties of Leather

By William T. Roddy and Robert M. Lollar

Department of Applied Science in Tanning Research
Foundation Tanners' Council of America
University of Cincinnati

Introduction

In the evaluation of the physical properties of leather many physical tests are utilized. It has often been questioned whether two or more tests may not be measuring the same property. If this is true, then some tests may be eliminated with a saving in time, effort, and leather.

The official methods of the American Leather Chemists Association as well as the Federal Specification KK-L-311 contain tests for measuring tensile strength, elongation and tearing strength. There are five methods for measuring tearing strength which are tongue, split, buckle and two variations of stitch tear strength. In a consideration of these tests by the American Leather Chemists Association Committee on Physical Tests it was agreed that a consideration should be given to determining if there is a correlation between certain of them. This paper reports the results of some work on this question.

Experimental

To obtain data from which we could determine the correlation of various physical properties throughout the entire side of upper leather, we cut 4 x 4 samples adjacent to each other from two sides. These were experimental tannages as stated later. On each 4 by 4 inch block stitch tear strength, grain crack strength and notch tear strength were determined. Notch tear, while not an official test for leather, was utilized because it required a small specimen. The sample is cut so that it has a wide V notch on the side as shown in Figure 1. Because of this shape the leather specimen tears at the same location each time. This test method is an official method of A. S. T. M. (D 624-48) and was developed for use on vulcanized rubber.

FIGURE 1.—Notch tear specimen.

Samples were also cut from the area to the rear of the kidney location from 72 sides of chrome-vegetable retan Army side upper leather on which tensile strength, tongue tear strength, stitch tear strength and small ball bursting strength were determined. These experiments were originally conducted to determine the characteristics of the new location proposed in the revision of the military specification MIL-L-3122 of July 20, 1951. The selection of this location by the military was based on work done by them on 30 sides using blocks of the entire sides in a similar manner to the sampling of the two entire sides we mentioned above. However, they used only 21 blocks as representative on each side whereas in this work 233 blocks were cut from one side and 175 blocks from another side. From the data obtained we have calculated the correlation coefficients between the various physical tests conducted to establish the inter-relationship of the physical properties determined.

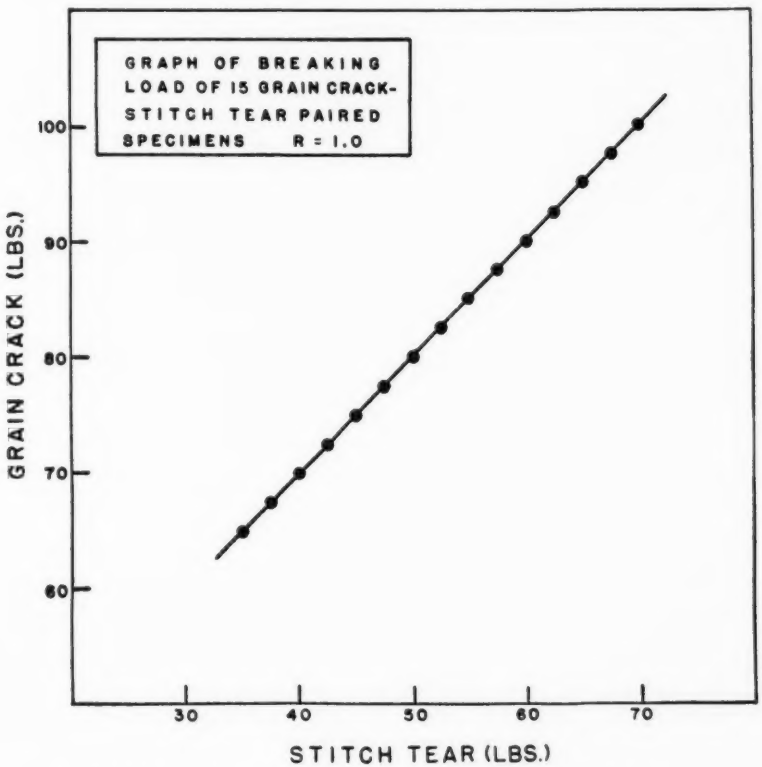

FIGURE 2.—Hypothetical example of grain crack versus stitch tear.

Results

To make a simplification of the interpretations which can be placed on correlation coefficients, a good starting point would be the hypothetical case where r is equal to 1.0. This is considered perfect correlation and means that values secured from the two methods are proportional as is shown in Figure 2.

The two measurements in this hypothetical example are grain crack strength and stitch tear strength. It is seen that as grain crack strength increases the stitch tear strength increases proportionately. When the points instead of falling on a straight line as shown tend to show a scattered spread, the correlation coefficient may drop as low as zero. Furthermore, negative correlation ranging from zero to minus one occurs when one variable tends to increase as the other variable decreases. If data of the nature shown in Figure 2 were actually secured, we would have no problem in reducing the

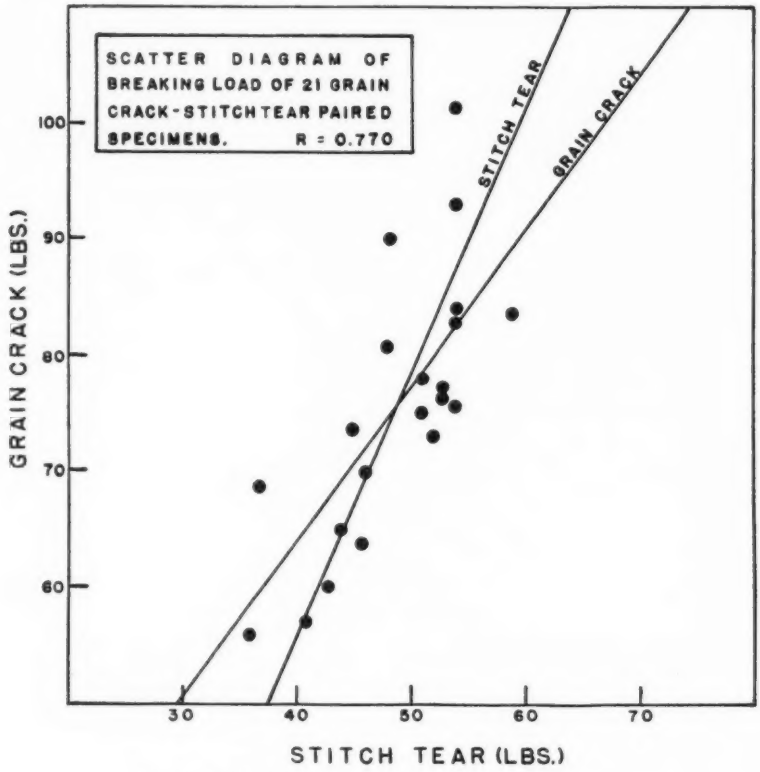

FIGURE 3.—Actual values of grain crack versus tear.

number of physical tests needed to determine leather characteristics and would thereby reduce the size of the area necessary. However, such is not the case when we analyze the actual strength measurements of leather.

To show what the correlation coefficients of leather represent, the graph in Figure 3 is given. This graph represents a scatter diagram of the comparison of grain crack versus stitch tear strength for the first row of blocks removed from a side one inch in from the backbone edge.

Examination of the respective points show that when grain crack strength in pounds is low the stitch tear strength in pounds is also low and as the grain crack strength is increased the stitch tear strength also increases, but it is not proportionate in each case. In addition to graphically illustrating the relation at each point, it is possible to calculate and draw regression lines to further emphasize the correlation. The r value of 0.77 for this set of data is the mutual relationship of the two regression lines or the geometric means of the slopes of the two lines and gives an indication of the linearity which exists. When grain crack strength is considered to be correct to within the range of one pound indicated by the circular dots in the graph, the regression line marked grain crack is obtained. When stitch tear strength is considered to be correct to within a one pound reading while making the test, the regression line marked stitch tear is obtained.

TABLE I

The Correlation between some Physical Properties of Leather over a Single Side

USXL—228 experimental tannage cut into 4 x 4 inch blocks over entire side. Rows of blocks and all test specimens oriented parallel to the backbone.

Tabular data are sample estimates of the Correlation Coefficients

Row Number	Stitch Tear vs. Notch Tear	Stitch Tear vs. Grain Crack	Notch Tear vs. Grain Crack
1	0.758	0.770	0.725
2	0.158	0.391	0.096
3	0.302	0.683	0.424
4	0.743	0.656	0.790
5	0.544	0.671	0.516
6	0.494	0.633	0.718
7	0.537	0.669	0.476
8	0.689	0.886	0.711
9	0.804	0.532	0.698
10	0.567	0.579	0.612
11	0.163	0.207	0.712
Average value of the Correlation Coefficient (Z Weighting, eliminating the non-significant values)			
	0.63	0.67	0.65

The perfect correlation where the r value or correlation coefficient would be as shown in the first graph which gave a straight line usually does not occur in measurement of products of biological origin. As the r value for this set of data is 0.77 there is deviation from linearity, and the regression lines indicate the relation between the two variates, grain crack and stitch tear.

The lower the r value or correlation coefficient for a given set of data the greater the variation between the two variates. The following results will show the size of a correlation which can be made of the physical properties determined in specimens from over an entire side versus a single specimen from the same location of many sides.

Table I shows the correlation between some physical properties of leather over a single side. The side selected was an experimental tannage where iron-titanium was used as the tannage and followed by vegetable retannage and having a grease level of 18 per cent. Blocks 4 x 4 inches over the entire side were tested for stitch tear strength, notch tear strength and grain crack strength, and all specimens were cut so the long axis of each specimen was parallel to the backbone. The data tabulated in this table are sample estimates of the correlation coefficients of each row as graphically illustrated in Figure 2. Rows 1 to 9 going from backbone to belly represent 22 blocks in each case. Row 10 had 18 blocks and row 11 had 17 blocks.

In the column stitch tear versus notch tear it is observed that r values as low as 0.158 for row 2 and 0.163 for row 11 are obtained. However, correlation is known to be highly variable. Furthermore, it is possible to use a Z-weighting technique [see Snedecor (3)] to take this variability into consideration. Using a Z-weighting calculation to eliminate the non-significant values, an average value of the correlation coefficient for this set of data would be 0.63. This is a statistically significant correlation; however, only 40 per cent [$(0.63)^2 \times 100$] of the variation is due to factors which influence the measurements similarly, while 60 per cent of the variance sources are different in the two measurements.

In the column stitch tear versus grain crack where the r values range from 0.207 to 0.886 with an average of 0.67 and in the column notch tear versus grain crack where the r values range from 0.096 to 0.790 with an average value of 0.65 after eliminating the non-significant values, the data again indicates correlation from the standpoint of statistics. However, in these two cases again only about 40 per cent of the variance is accounted for in the two properties compared in each instance. The average correlation coefficient calculated by use of the Z-weighting technique is noted not to differ significantly from any individual sample estimates of the correlation coefficients given in each column in Table I.

Table II shows the correlation between the physical properties over another side of leather. The side in this case was sulfonyl chloride tannage followed by a vegetable retannage. The side was cut into 4 x 4 inch blocks over the entire side and the specimens for test cut parallel to the backbone. The

tabular data are again sample estimates of the correlation coefficients for each row. Row 1 to 6 represents 21 blocks cut from tail to head in each case and the row going from backbone to belly. Row 7 represents 20 blocks; row 8 had 19 blocks and row 9 had 10 blocks.

TABLE II

The Correlation between some Physical Properties of Leather over a Single Side

USXL–230 experimental tannage cut into 4 x 4 inch blocks over entire side. Rows of blocks and all test specimens oriented parallel to the backbone.

Tabular data are sample estimates of the Correlation Coefficients.

Row Number	Stitch Tear vs. Notch Tear	Stitch Tear vs. Grain Crack	Notch Tear vs. Grain Crack
1	0.249	0.303	0.823
2	0.578	0.562	0.638
3	0.737	0.755	0.784
4	0.829	0.762	0.632
5	0.818	0.898	0.835
6	0.465	0.742	0.707
7	0.500	0.495	0.059
8	0.731	0.413	0.213
9	– 0.321	0.132	0.641
Average value of the Correlation Coefficient (Z Weighting, eliminating the non-significant values)			
	0.69	0.73	0.74

In the column stitch tear versus notch tear, it is seen that r values of minus 0.321 to a positive value of 0.829 occur. The bottom row in the belly region gave a negative correlation. Using a Z-weighting technique and eliminating the non-significant values, the best average value of correlation for this set of data is 0.69. This is a statistically significant correlation, but squaring the value would indicate that only 48.5 per cent of the variance is accounted for in their inter-relationship, while the remainder is due to independent error sources.

The relation between stitch tear versus grain crack and notch tear versus grain crack is again indicated by the correlation coefficients obtained. In both columns it can be seen that in a given row the correlation may be far below the average, but the average correlation coefficients are about the same as that obtained in the first column. These average values of the correlation coefficients indicate that this side is much the same as the first side reported on the basis of correlation. The data show that there is inter-relationship, but one must be satisfied that only half of the variance is accounted for in their inter-relationship. While it is typical of data obtained from other

products of biological origin, it certainly would not be possible to use a single test to obtain all of the characteristics of the finished leather within any reasonable prediction.

TABLE III

The Correlation between some Physical Properties of Leather.

Six tanners of chrome vegetable retan Army shoe upper leather supplied blocks of leather from the area to rear of the kidney from twelve sides of their production.

Tabular data are sample estimates of the Correlation Coefficient

Tanner	Tonge Tear vs. Stitch Tear	Tongue Tear vs. Tensile Strength	Tongue Tear vs. Small Ball Burst	Stitch Tear vs. Tensile Strength	Stitch Tear vs. Small Ball Burst	Tensile Strength vs. Small Ball Burst
E	0.81	0.89	0.83	0.88	0.86	0.88
V	0.78	0.45	0.62	0.65	0.73	0.91
A	0.69	0.48	0.67	0.64	0.86	0.80
I	0.76	0.57	0.48	0.69	0.66	0.91
S	0.21	0.76	0.57	0.45	0.63	0.77
D	0.50	0.46	0.47	0.35	0.35	0.79
	Average value of Correlation Coefficient (Z Weighting)					
	0.66	0.64	0.63	0.65	0.72	0.85

The results in Table III further emphasize the point of possible prediction based on a single physical test. In this table the correlation between tongue tear, stitch tear, tensile strength and small ball burst strength on leathers from 6 tanners of chrome-vegetable retan Army shoe upper leather is given. The area to the rear of the kidney from 12 sides of their production was used in each case.

The correlations considered from the 6 leathers coded E, V, A, I, S, and D are tongue tear versus stitch tear, tensile strength and small ball burst, stitch tear versus tensile strength and small ball burst and tensile strength versus small ball burst. In this case leather from tanner E shows the best corelation coefficients in all inter-relationships while leather from tanner D has about the lowest set of values in all cases. The average value of the correlation coefficient was calculated using the Z-weighting technique to show that the values obtained on the different tanners leathers all came from the same statistical population and to show also the relation of each tanner's leather to the average.

The average values of the first five columns are of the same magnitude as those reported from the two sides where similar inter-relationships were considered. The average value for tensile strength versus small ball burst is slightly higher. All of the correlation coefficients obtained in this work are

very similar to those obtained by the Quartermaster Research and Development Branch [2] in their extensive study of a series of experimental leathers where the test specimens in each case were taken from an area which reflects the side average most accurately for the particular physical property studied.

Summary

In summary the present research indicates that there is inter-relationship among the physical tests for leather considered in this report, but that only half of the variance is accounted for in the inter-relations considered. The results in Table III for tanner E show that while it might be possible to have good correlation in all inter-relations, that most of the leathers, in table III, do not meet this requirement. Therefore, it would not be wise to reduce the number of physical tests unless it is certain that the inter-relations of the various physical tests have been established. Based on the evidence presented, the physical tests designed for leather, while measuring common characteristics in some instances, reflect different variance sources sufficiently to warrant the retention of the presently used test methods.

Bibliography

1. Mann, C. W., Randall, E. B., Mandel, J., Kilduff, T. J., and Charles, A. M. The Sampling of Side Upper Leather. *J.A.L.C.A.* **46**, 248 (1951).
2. Mann, C. W., Mandel, J., Steel, M. N., and Kanagy, J. R. Sampling of Side Upper Leather II. *J.A.L.C.A.* **47**, 352 (1952).
3. Snedecor, G. W., "Statistical Methods." Iowa State College Press, Ames, Iowa. Fourth Edition, 1946. Page 150.

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The Chemistry of Vegetable Tannins

VI. Physical Data

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Four purified vegetable tannins have been selected and physical measurements made on them in solid form and in solution. Some of the data obtained are presented in this article. The tannins were:

Quebracho	(Q)
Wattle	(W)
Mangrove	(M)
Chestnut	(C)

The quebracho used was substance A previously described[1]. The wattle purification has also been reported[2]. The preparation of the mangrove and chestnut will be discussed in later publications.

Molar Refraction

The molar refraction of a compound is defined as the product of two factors, the apparent molar volume and a term involving the refractive index:

$$R = \frac{M}{d}\,\frac{n^2-1}{n^2+2}$$

Its value depends on the wavelength of light used to measure the refractive index.

Since the molar refraction is both an additive and constitutive property, refraction equivalents have been computed for some elements and bonds. Thus the computed value may be compared with the value obtained by measuring the refractive index and density and some information obtained as to whether a structure suggested for a substance fits the data.

If the radiation employed were of infinite wavelength and the molecules were perfectly conducting spheres, theory states that the molar refraction would represent the actual volume of the molecules in one mol of substance as compared with the apparent volume. For convenience, however, measurements are made with visible light and the data obtained represent an approximation. The refractive index factor may be considered to reflect the relation between apparent and true molar volume. The densities of the tannins in solid form were measured by flotation and the apparent volume calculated:

	Mol. Wt. (M)	Density $d\,\frac{25.5}{15}$	Apparent Volume (cc.) $\frac{M}{d}$
Q H_2O	594.6	1.393	427
W 1.5 H_2O	605.5	1.465	413
M 2.5 H_2O	623.6	1.479	422
C 2.0 H_2O	676.5 tentative	1.600	423

Solutions of the tannins in absolute alcohol were prepared and the refractive index differences between solution and solvent measured at 25.5°C. on a Phoenix Precision Differential Refractometer at three wavelengths using the sodium D line and the mercury green and blue lines. Five readings were taken of each measurement and the readings averaged.

	Index Error	Wave length (A)
NaD	+ 0.069 ± 0.004	5893
HgG	+ 0.073 ± 0.003	5460
HgB	+ 0.070 ± 0.004	4358

Tannin Solutions	Conc. Gm./100 cc.
Q	0.2000 ± 0.0002
W	0.2000 ± 0.0002
M	0.1525 ± 0.0002
C	0.1615 ± 0.0002

	Refractometer differences	Corrected for index error
QD	−0.396 ± 0.007	−0.465 ± 0.011
QG	−0.413 ± 0.006	−0.486 ± 0.009
QB	−0.430 ± 0.005	−0.500 ± 0.009
WD	−0.384 ± 0.006	−0.453 ± 0.010
WG	−0.386 ± 0.003	−0.459 ± 0.006
WB	−0.381 ± 0.007	−0.451 ± 0.011
MD	−0.203 ± 0.005	−0.272 ± 0.009
MG	−0.212 ± 0.005	−0.285 ± 0.008
MB	−0.228 ± 0.003	−0.298 ± 0.007
CD	−0.168 ± 0.006	−0.237 ± 0.010
CG	−0.162 ± 0.003	−0.235 ± 0.006
CB	−0.216 ± 0.007	−0.286 ± 0.011

The factor to convert the observed readings to refractive indices assuming linearity with concentration was: $\frac{(-9.25 \pm 0.05)\ 10^{-4}}{\text{conc. (gm./cc.)}}$

	Refractive index differences (pure solute minus pure solvent)	Refractive index of pure solute (R. I. of solvent = 1.360 ± 0.001)
QnD	0.215 ± 0.005	1.575 ± 0.006
QnG	0.225 ± 0.004	1.585 ± 0.005
QnB	0.231 ± 0.004	1.591 ± 0.005
WnD	0.210 ± 0.005	1.570 ± 0.006
WnG	0.212 ± 0.003	1.572 ± 0.004
WnB	0.209 ± 0.005	1.569 ± 0.006
MnD	0.165 ± 0.005	1.525 ± 0.006
WnG	0.173 ± 0.005	1.533 ± 0.006
WnB	0.181 ± 0.004	1.541 ± 0.005
CnD	0.136 ± 0.006	1.496 ± 0.007
CnG	0.135 ± 0.003	1.495 ± 0.004
CnB	0.164 ± 0.006	1.524 ± 0.006

Since the refractive indices of the pure solutes were the same in nearly all cases due to the limited accuracy of the method and since refraction equivalents are not available for the green and blue lines the factors were computed for the sodium line only.

Factor (F) $\frac{n^2D - 1}{n^2D + 2}$	Reciprocal (1) factor (F)	Molar refraction (cc.)	Molar refraction calculated from refraction equivalents (7) (cc.)
Q 0.330	3.0	141 ± 1	147
W 0.328	3.0	139 ± 1	146
M 0.307	3.3	130 ± 1	150
C 0.292	3.4	124 ± 1	(tentative)150(tentative)

In calculating the molar refraction from refraction equivalents the water of crystallization was treated as part of the molecule. The actual effect of such water molecules and how they should be treated has apparently not been definitely established, nor has the effect of hydrogen bonding in phenols been established. In order to gain some insight as to the possible direction and magnitude of such effects the molar refractions of hydrated and anhydrous phloroglucinol were measured and compared with the calculated values, viz.:

	Found	Calc.
P	28.2	30.9
P $2H_2O$	35.8	38.3

As with the tannins the calculated value appears to be higher than the observed and the ratios of the former to the latter are

Q	W	M	C	P	P$2H_2O$
1.04	1.05	1.15	1.21	1.10	1.07

Since the actual values in the cases of quebracho and wattle do not seriously differ from the calculated values of the molar refraction for such large molecules this work lends support to the structures assigned to them. Other structures in general either have the same or greater calculated values and thus differ in greater degree from the observed values. The results may be brought into somewhat closer agreement by reducing the calculated values by the benzene ring decrement (0.17 cc. per ring) and the tetrahydropyran ring decrement (0.23 cc. per ring).

The average error in the calculated versus found values for the two samples of phloroglucinol was 8.3%. For quebracho the error was 4.3% and for wattle 5.0%.

In the cases of quebracho and wattle the apparent molar volume as indicated by the reciprocal factor is exactly three times that of the true volume or molar refraction. It is interesting that Lorenz and Herz [3] worked out a relation indicating that the zero point molar volume of gases and liquids should be three times the refractive index for most common substances and found an average deviation of 13%. Apparently a similar relation for solids has not been evolved.

Molecular Volume

The value of the molar refraction for quebracho previously given (141 cc.) cannot be the true molar volume; first, since the molecule is not a sphere, and second, even if it were, the computed radius of such a sphere would have the value 3.82A which is quite small.

The apparent molar volume obtained from the density is 427 cc. This gives a volume for a single molecule of 709A^3. If the molecule were spherical, its radius would be 5.53A. A model of the molecule of quebracho having the structure suggested previously [4] in which the two resorcinol nuclei are joined by a bond can be laid out in a long flat sheet in which the principal deviations from planarity are the terminal methyl and certain hydroxyl groups. By drawing a smooth oval about this plane and measuring its area with a planimeter and dividing this value (254A^2) into the volume (709A^3), a value of 2.8A is obtained as the thickness of the molecule. The benzene rings in the models (Fisher-Hirschfelder-Taylor) have a thickness of 2.67A apparently based on the idea that the van der Waals radius is about twice the single bond covalent radius (0.67A). The value 2.8A fits well with the fact that the molecule has some projections and is not perfectly planar.

In an effort to obtain some idea of the volume represented by the model, it was placed in water and found to displace 442A^3. (1A = 1 cm.). This method, however, does not exclude the volume within the benzene rings; and, consequently, the displaced volume is low. In a further effort to approximate the molecular volume, the model was sprayed with a solution of resin which webbed across the vacant spaces and covered it with a tightly fitting, water-repellent, glovelike coating. The hydrogen atoms appeared as strong projections of the surface. By displacement the coated model was found to have a volume of 600A^3 (1A = 1 cm.). This is in very good agreement with the molecular volume of 709A^3. If it were possible to cover the model with a smooth envelope to approximate its volume, the values would be very close indeed.

The volume of a cylinder of rotation having as altitude the length of the molecule in its longest planar form and as diameter the average width of the plane is 1350A^3. Alternatively, the model may be folded and the catechol planes brought parallel giving a box-like shape. The total volume of this figure is 1320A^3. The additional space in each of these corresponds to approximately one more molecule of the compound and in the case of the planar

model the total volume equals that of two molecules placed adjacent plane to plane. The planar form would be conducive to hydrogen bonding to form a dimer in cases where strong hydrogen bonding is possible as here. Even in the methylated derivative [1], the molecular weight in acetone appeared to indicate possible dimerisation.

Surface Tension

The surface tensions of the four tannins used in the previous experiments were measured in water solution at a concentration of 2% by dissolving the tannins in water above 50°C. and allowing them to come to the temperatures indicated. The solutions were then diluted to 1% and remeasured. After standing 17 hours at 53°C., they were measured again, then diluted to 0.5% and the final readings taken. The data obtained from a Du Noüy Interfacial Tensiometer are given below:

Tannin	Conc. %	Dynes/cm.	Temp. °C.
W	2.0	55.3 ± 0.2	30.8
C	2.0	62.4 ± 0.3	30.2
Q	2.0	59.8 ± 0.3	31.6
Q	2.0	59.5 ± 0.2	32.2
M	2.0	72.5 ± 0.3	30.4
W	1.0	56.9 ± 0.1	35.8
C	1.0	62.1 ± 0.2	35.1
Q	1.0	58.1 ± 1.6	31.5
M	1.0	69.0 ± 0.2	33.9
	After standing 17 hours at 53°C.		
W	1.0	59.3 ± 0.6	28.5
C	1.0	60.6 ± 0.1	32.4
Q	1.0	60.2 ± 0.6	31.6
M	1.0	69.2 ± 0.2	29.2
W	0.5	61.9 ± 0.2	30.5
C	0.5	64.0 ± 0.2	33.2
Q	0.5	61.3 ± 0.4	32.6
M	0.5	70.1 ± 0.8	31.4

For comparison the surface tension of water is given [5]:

Temp. °C.	Dynes/cm.
28	71.50
29	71.35
30	71.18
35	70.38

The data indicate no very large effect due to aging nor any important effect due to concentration in the range studied. The ability to reduce the

surface tension of water at a concentration of 1 and 2 per cent followed the order:

$$W > Q > C > M$$

At 0.5% the order was:

$$Q > W > C > M$$

Some difficulty was experienced in making the measurements on quebracho and mangrove as air oxidation caused a slight tendency toward skinning on the surface forcing the readings to be made as quickly as possible.

According to Fischer and Gans [6] most surface active agents in 1% solution have a surface tension in the range of 28-38 dynes per centimeter. The values found for the four tannins tested show that they are not strongly surface active.

Viscosity

Solutions of the four tannins used in this work were prepared in water and their viscosities measured with a Hoeppler Viscosimeter at two concentrations using both steel and glass balls to given different rates of shear. The data obtained are given below:

Tannin	% Conc.	Temp. °C.	Ball	Viscosity (Cps.)
Q	1.0	52.8	S	0.72 ± 0.04
Q	1.0	52.8	G	0.61 ± 0.01
Q	0.5	52.4	S	0.70 ± 0.03
Q	0.5	51.9	G	0.58 ± 0.01
W	1.0	52.7	S	0.70 ± 0.02
W	1.0	52.1	G	0.58 ± 0.01
W	0.5	52.2	S	0.70 ± 0.02
W	0.5	51.7	G	0.55 ± 0.01
C	1.0	52.0	S	0.71 ± 0.02
C	1.0	51.5	G	0.58 ± 0.01
C	0.5	51.3	S	0.71 ± 0.02
C	0.5	50.1	G	0.58 ± 0.01
M	1.0	52.0	S	0.69 ± 0.02
M	1.0	52.0	G	0.62 ± 0.02
M	0.5	51.9	S	0.68 ± 0.02
M	0.5	52.2	G	0.57 ± 0.01

For comparison purposes the viscosity of water is given [5]:

Viscosity (Cps.)	Temp. °C.
0.568	48
0.549	50
0.532	52
0.515	54

The solutions showed equal or higher viscosities at 1.0% than at 0.5%. They all had higher values than water but at the lower rate of shear the differences were small. The values are related as follows:

High shear – 1.0% – Q > C > W >M
High shear – 0.5% – C > Q= W >M
Low shear – 1.0% – M> Q> W =C
Low shear – 0.5% – Q = C> M > W

The increase of viscosity with shear indicates dilatancy. This may be due to the formation of a layer-like structure by the lining up of the molecules during shearing. The hydrogen bonding of a sheet-like molecule would be expected to enhance this effect.

Summary

1. The refractive indices of four tannins have been measured at three wavelengths.
2. The molar refractions have been determined and compared with values calculated from refraction equivalents. The values are noticeably close in the cases of quebracho and wattle.
3. The thickness of a molecule of quebracho has been computed from the molecular volume and found to be in excellent agreement with that determined from a model.
4. The approximate volume of a model of a quebracho molecule has been measured and found to agree satisfactorily with the computed volume.
5. The ease of dimerization of quebracho due to hydrogen bonding has been indicated by computation of the volume of two molecules either placed parallel with their plane faces adjacent or folded and mutually intersecting.
6. The surface tensions of solutions of four tannins have been measured. The data indicate that the tannins are not strongly surface active.
7. The viscosities of solutions of four tannins have been measured. They all showed slightly higher viscosities than pure water. Increased viscosity with shear signified the presence of dilatancy. This appeared to indicate some formation of structure in solution due to shearing.

Bibliography

1. Putnam and Gensler, *J. Am. Leather Chemists' Assoc.*, **46**, 613 (1951).
2. Putnam and Gensler, *J. Am. Leather Chemists' Assoc.*, **47**, 478 (1952).
3. Lorenz and Herz, *Z. Anorg. Allgem. Chem.* **142**, 80 (1925).
4. Putnam, *J. Am. Leather Chemists' Assoc.*, **47**, 474 (1952)
5. Lange, Handbook of Chemistry, Handbook Publishers, Sandusky, O. (1946).
6. Fischer and Gans, *Ann. N. Y. Acad. Sci.* **46**, Art. 6, 371 (1946).
7. Eisenlohr, *Z. physik. Chem.* **75**, 585 (1910).

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Acetyl Determination Methods For Substituted Black Wattle Tannins

By D. G. Roux

Putnam and Gensler recently developed a drastic "peracetylation" technique [1] by means of which they claim such complete substitution of quebracho and wattle tannins [2], that all the oxygen present in both substances could be accounted for as hydroxyl groupings. Their "peracetylated" wattle tannin, for example, apparently contains a higher proportion of acetyl groups (47.4 – 48.7%) than those acetylated wattle tannins prepared by the author [3] with the conventional acetyl chloride/pyridine mixture (37.5 – 38.3% acetyl), and by other investigators [4, 5] using both the sodium acetate/acetic anhydride and acetyl chloride/pyridine techniques successively (38.1 – 41.3% acetyl).

The repetition of Putnam and Gensler's acetylation technique on the whole tannin (polyphenolic) fraction, from which the gums and sugars had been carefully removed [6], failed to give the desired increase in acetyl value when carried out in these laboratories, but showed that after the first reductive stage, the wattle tannin was almost completely substituted to the maximum value obtainable by us. d-Catechin was similarly completely converted to the fully substituted penta-acetyl derivative at this stage, and was also recovered unchanged after the prolonged reaction in the second step of Putnam and Gensler's "peracetylation" method.

Subsequently, however, it has become evident [7] that the above 8 - 10 per cent difference in acetyl values obtained, was most likely due to different methods of acetyl determination. Putnam and Gensler used an alkaline hydrolysis method similar to that described by Clark [8], whereas we have consistently used Matchett and Levine's acid hydrolysis technique [9] which also involves the trans-esterification principle.

Although alkaline hydrolysis techniques have been used effectively for the estimation of acetyl groups in stable carbohydrate acetates, including the more difficulty hydrolised groups present in acetylated starch and cellulose [10], high values are obtainable from acetylated glucose due possibly to the degradation of glucose to lactic acid [11]. For this reason Whistler and Jeanes [10] used sodium methoxide at room temperature for the hydrolysis of acetyl groups of labile sugars. Similarly, because of the far greater instability of phenolic and polyphenolic nuclei, the alkaline hydrolysis method cannot be used for the quantitative estimation of phenolic acetates. Erdmann and Schultz [12] have shown that acetylhaematoxylin yields formic acid when digested with dilute boiling alkali, and Stephen [4] has demonstrated that both the acetylated and unsubstituted black wattle tannins, if boiled with 0.25*N* alkali, liberated much acid titrating between pH = 3.1 and 7.8. He conse-

quently used Matchett and Levine's acid hydrolysis and trans-esterification method for the acetyl estimation of substituted black wattle tannins. More recently Shuttleworth [13] established by potentiometric titrations that d-catechin, catechol, pyrogallol and black wattle tannins (when autoclaved with 0.1 *N* alkali at 240°F for 1 hour under identical conditions) all gave rise to varying quantities of acids which titrate between pH = 3 and 7.

From the above evidence it is obvious that phenolic nuclei, particularly the very unstable orthodihydroxy and orthotrihydroxy species, are easily decomposed under alkaline conditions to form acids of the same "acidic strength" as acetic acid. Under acidic conditions, by contrast, the polyphenols show a tendency towards self-condensation or "phlobaphene" formation, and the Matchett and Levine transesterification method was found to give quantitative results when standardised against pentacetyl-d-catechin and triacetylpyrogallol. It is probably for the above reasons that Perkin [14] and Freudenberg [15] used similar acid hydrolysis methods for assessing the acetyl content of substituted polyphenols.

In more recent work on mangrove tannin [16] Putnam accually established that unsubstituted polyphenols such as catechin and fisetin give apparent "acetyl" values by the alkaline hydrolysis method, but did not appear to realize the significance of this in relation to the method of acetyl estimation. He considered that the acetic acid formed might possibly originate from the presence or formation of a pyrone-like structure. His data, however, further confirms that the decomposition of unstable phenolic nuclei under alkaline conditions, is probably responsible for the formation of formic and acetic acids. Thus 3-hydroxyflavone, containing stable phenyl but no phenolic nuclei, gives no "acetyl" value, whereas fisetin and d-catechin (containing catechol, resorcinol and phloroglucinol units) have apparent acetyl contents of 3.6 and 7.8 per cent respectively. Similarly the instability of kojic acid, whose dimethyl derivative is converted to formic and acetic acids on alkaline hydrolysis [17], probably accounts for the 5.5 per cent "acetyl" found by Putnam. The dihydropyrane structure appears to be more stable, and it is considered improbable that the pyrane and pyrone rings in 2-phenylbenzopyrane or 2-phenylbenzopyrone units, in which benzenoid rings furnish the double bonds, would be primarily responsible for yielding acetic acid under alkaline refluxing conditions.

As previously stated [3], and from the above facts, it is evident that black wattle tannins contain a high proportion of oxygen which cannot be substituted. This oxygen is probably mainly comprised of ether links, although tertiary aliphatic hydroxyl groups could also be present. The latter possibility is considered unlikely, however, as added reactivity appears to be conferred on tertiary aliphatic hydroxyl groups where these are present in close proximity to phenolic nuclei, e. g. as in brazilin and haematoxylin.

Summary

The alkaline hydrolysis method of acetyl estimation as used by Putnam and Gensler, furnishes erroneously high results due to the partial decomposition of labile phenolic nuclei under the experimental conditions, resulting in the consequent formation of volatile aliphatic acids. This method has been shown to be responsible for the abnormally high degree of substitution claimed by these authors for black wattle tannins.

Acid hydrolysis techniques as used by Perkin, Freudenberg and Matchett and Levine appear to be more satisfactory and yield quantitative results with triacetylpyrogallol and pentaacetyl-d-catechin.

Putnam and Gensler's data on quebracho, wattle and mangrove tannins must, therefore, be reviewed in the light of these facts.

References

1. Putnam and Gensler, *J. Am. Leather Chem. Assoc.* **46**,613 (1951).
2. Putnam and Gensler. *J. Am. Leather Chem. Assoc.* **47**, 478 (1952).
3. Roux. *J. Soc. Leather Trades' Chemists*, **34**, 129 (1950).
4. Stephen. Ph. D. Thesis. Univ. of Cape Town (1946).
5. Lowitt. M. Sc. Thesis. Univ. S.A. (1947).
6. Roux. *J. Soc. Leather Trades' Chemists* (in press).
7. Putnam. Private Communication.
8. Clark. *Ind. Eng. Chem. Anal. Ed.* **8**, 487 (1936). *ibid.* **9**, 539 (1937).
9. Matchett and Levine. *ibid.* **13**, 98 (1941).
10. Whistler and Jeanes. *ibid.* **15**, 316 (1943).
11. Clarke and Christensen. *ibid.* **17**, 335 (1945).
12. Erdmann and Schultz *Annalen.* **216**, 234 (1882).
13. Shuttleworth. Leather Ind. Research Bull. No. 99 (1950).
14. Perkin. *J. Chem. Soc.* **87**, 107 (1905).
15. Freudenberg. *Annalen.* **433**, 230 (1923).
16. Putnam. *J. Am. Leather Chem. Assoc.* **47**, 512 (1952).
17. Yabuta. *J. Chem. Soc.* **122**, 939 (1922).

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The Effect of Microbiological and Pancreatic Bates on Limed Skins

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The action of bating materials upon skins and hides has been the subject of study and controversy for many years. Anderson [1] has reviewed the major mechanisms which have been advanced to explain the bating phenomena.

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The conventional bating materials have employed enzymes secured from pancreatic extracts; however, more recently, microbiological enzymes have been used in bating. Some of these enzymes have not given the same bating action that is obtained by the pancreatic bating materials. Hence, comparative studies of the action of microbiological enzymes and tryptic enzymes in bating may be informative and aid in our understanding of the mechanism of bating.

This study has compared the action of a particular microbiological bating enzyme (P 166) with a particular pancreatic bating enzyme (Oropon CS or WN-4). The bating efficiency has been compared by the methods of Moore [5] and of McLaughlin and Wilson [3]. Further, emphasis was placed upon an examination of the hydroxyproline content of spent bate liquors and the bated pieces in an attempt to estimate the influence of such bating upon the collagen of the skin pieces used. Since collagen is unique in its hydroxyproline content, an assay for hydroxyproline permits a determination to be made of the collagen content of any substrate. Because it is sometimes stated that one mechanism of bating is the purification of the collagen, and perhaps the removal of denatured collagen formed before bating, it seemed worthwhile to follow the collagen balance of the skin during the bating.

For comparative purposes, the two bating enzyme preparations were compared to three other enzyme systems. The first was a system comparable to U.S.P. pancreatin, which therefore contained proteolytic enzymes as well as lipase. Second, a tryptic type enzyme was prepared in which the enzyme complement had been narrowed to the tryptic-type enzymes. Finally, crystalline trypsin was used. These enzymes were prepared by the Pabst Laboratories, and were diluted to a uniform proteolytic value on inert substrates before being supplied to us.

Analytical Procedures

The particular bating procedures will be described in conjunction with the presentation of the experimental data. However, the following procedures were employed throughout the work to evaluate and control the bating action.

1– The Moore procedure [5] and the McLaughlin-Wilson procedure [3] for the evaluation of bating materials were employed.

2– Deliming of the calfskin squares (1 inch) prior to bating was accomplished by stirring 50 grams of the squares with 3.1 ml. of 2.8 per cent hydrochloric acid in 178 ml. of distilled water until the surface lime was neutralized. Then, 18.7 ml. of a 4 per cent solution of boric acid was added, and the solution brought to 95° F. prior to the addition of the bating material. Bating was then continued as discussed later.

3– Hydroxyproline Assay for Collagen.

The filtered spent bate liquors, the bated skin squares, and the hot water extracts of these squares were analyzed for their hydroxyproline content by the method of Neuman and Logan [6]. The method depends upon the oxidation

of the hydroxyproline to a pyrrole derivative in a basic copper solution, using hydrogen peroxide as the oxidant, followed by the development of a colored solution by the addition of dimethylaminobenzaldehyde after acidification. Spectrophotometric reading of the developed color makes it possible to estimate the hydroxyproline content of any protein hydrolyzate. This hydroxyproline value is converted to a value for collagen by use of the fact that collagen contains 13.3 per cent hydroxyproline. The hydrolyzates were obtained by the use of constant boiling hydrochloric acid under reflux for 16 hours. The method is very sensitive, requiring considerable dilution of the hydrolyzates. Thus, the hydrolyzate from 1 gram of collagen is diluted to 5 liters, and only 1 ml. of this diluted hydrolyzate is used for color development.

Experimental Results

The data secured from the use of the Moore procedure to compare the action of a pancreatic bate (Oropon CS) to a microbiological bate (P 166) are presented in the statistical table appearing in Table 1. A randomized block

TABLE 1

Statistical Analysis of Physical Test Results
Moore Procedure

A. Coefficient of Friction Test

Source of Variance	Sums of Squares	Degrees of Freedom	Mean Squares	F Values
Between Bates	.00633	1	.00633	2.2
Between Skins	.17091	3	.05697	20.1**
Interaction of Bates and Skins	.00145	3	.00048	
Residual	.11302	40	.00283	
Total	.29171	47		

B. Per Cent Compressibility

Between Bates	239.860	1	239.860	7.9**
Between Skins	1339.727	3	446.576	14.9**
Interaction of Bates and Skins	125.396	3	41.798	
Residual	1205.26	40	30.13	
Total	2910.243	47		

C. Air Permeability

Between Bates	96.3	1	96.3	1.1
Between Skins	13566.3	3	4522.1	53.0**
Interaction of Bates and Skins	1435.1	3	478.37	5.6
Residual	3384.0	40	84.6	
Total	18481.7	47		

**Indicates a statistically significant difference.

series of experiments were performed. Eight pieces were taken from each of four limed calfskins for bating under identical conditions with each of the two enzymes. One per cent of the bating materials was used, and bating was carried out at a pH of 8.5 for 1.5 hours at 95°F. with a solution to stock ratio of 4 to 1.

The results in Table I illustrate that the microbiological bating material has performed very similarly to the pancreatic bating material, as evaluated by the Moore procedure. This procedure measures the slipperyness of the grain, the compressibility of the piece, and its permeability to air, three properties recognized by the practical tanner as characteristic properties which are modified during bating. The ability of different skins to be bated is variable, and the data in Table I demonstrate this since the variance due to skins is significant. All three of the evaluatory tests show that the four skins were bated to different extents by both of these bating materials. In contrast, the bating action of the two different enzymes is so similar, that only the compressibility test showed a significance difference in the bate variances. In this case the microbiological enzymes produced pieces that were more compressible than those from the pancreatic enzyme. This would imply a more extensive bating action, or perhaps a greater depletion of the skins as a result of the bating action by the microbiological enzyme. However, in summary, it may be noted that these two enzymes are so similar that the difference between them is less than the differences between the bating characteristics of the four skins employed. For practical purposes, therefore, these enzymes should give similar bating action.

The procedure of McLaughlin and Wilson [3] evaluates the bating efficiency of an enzyme preparation in terms of the amount of nitrogen solubilized under a specific set of test conditions. Their article presents the comparison of two bating materials, one used successfully and another unsucessfully in a calf skin tannery. The bate preparation giving satisfactory results shows a continuously increasing level of nitrogen solubilization, reaching somewhat more than 80 mg. of nitrogen dissolved in six hours. On the other hand, the unsatisfactory bate preparation solubilized only about 50 mg. of nitrogen in the same time period. Table II presents the data secured when this method was employed to evaluate the enzymes used in this work. The particular laboratory procedure followed was that given by Merrill [4], and employed hydrochloric acid and boric acid for deliming as discussed previously. This was necessary to prevent errors due to ammonia nitrogen from the delimer. Further, the pancreatic bate employed had to be changed to Oropon WN-4 to eliminate the ammonium sulfate. The pancreatic bate was found to be approximately four times as strong as the microbiological bate; therefore, it was decided to use the pancreatic bate at the 0.1 per cent level, and the microbiological bate at the 0.4 per cent level. Further, the three supplementary enzyme preparations were sufficiently concentrated to permit them to be used at the 0.1 per cent level.

TABLE II

Nitrogen Solubilized in McLaughlin Wilson Procedure

Enzymatic Preparation	Conc. %	Bating Time 1	2	3	4½	6 hrs.
		Mg. of N in Bate Liquors from 50 gms. of Skin				
Water Control		16.8	17.7	——	——	19.1
Pancreatic commercial bate (Oropon WN-4)	0.1	27.8	37.4	33.0	37.4	46.0
Microbial bate 166	0.4	27.0	32.8	34.7	36.5	40.9
Pancreatic Type	0.1	28.8	34.0	35.6	40.6	45.7
Tryptic Type	0.1	25.8	28.0	31.8	30.8	34.8
Crystalline Trypsin	0.1	28.0	30.7	37.5	36.3	40.5

The data in Table II shows that all of the enzymes used in this work are more nearly comparable to the satisfactory bate than to the unsatisfactory bate evaluated by McLaughlin and Wilson. The poorest results were secured from the tryptic-type enzyme. The microbiological bate is very comparable to the pancreatic bate, except that at the six hour period, its nitrogen solubilization is somewhat lower. However, it has been our experience that this method does not reproduce sufficiently well to permit any conclusion to be drawn concerning the difference between the pancreatic enzyme and the microbiological enzyme. The data in Table II would seem to indicate that the two enzyme preparations are similar in bating efficiency, a conclusion in agreement to that shown by the Moore procedure earlier.

TABLE III

Collagen in Spent Bate Liquors
Hydroxyproline Assay

Enzymatic Preparations	Conc. %	Bating Time 1	2	3	4½	6 hours
		Mg. Collagen from 50 G. skin				
Water Control	——	0.0	1.88	——	——	3.13
Pancreatic commercial bate (Oropon WN-4)	0.1	1.88	5.64	5.64	6.92	8.8
Microbial bate (P166)	0.4	3.76	5.64	3.76	9.4	21.3
Pancreatic type	0.1	2.5	2.5	5.64	7.52	18.4
Tryptic type	0.1	1.25	2.5	7.52	6.9	12.2
Crystalline Trypsin	0.1	1.88	4.38	5.64	6.3	16.8

Table III presents the data from the hydroxyproline assay of the spent bate liquors. It is obvious that the bating enzymes have removed small amounts of collagen from the skins, and that these amounts are in excess of the amount removed by water alone. However, the amount removed is very small (less than 0.1 per cent of the total collagen), so that it does not seem that removal of denatured collagen is a very significant function in bating.

TABLE IV

Total Collagen Content of Bated Skins
(10% H_2O in Skin)

Enzymatic Preparation	Conc.	Bating Time 1	2	3	4½	6 hours
		Mg. Collagen from 50 G. skin				
Water Control	——	765	840	——	——	810
Pancreatic Commercial Bate (Oropon WN-4)	0.1	730	925	900	865	805
Microbial Bate (P 166)	0.4	780	890	825	890	845
Pancreatic Type	0.1	795	875	835	930	870
Tryptic Type	0.1	770	875	790	895	845
Crystalline Trypsin	0.1	770	795	905	908	900

Table IV shows the results from the analysis of the air equilibriated, solvent dehydrated bated skin pieces for their collagen content as revealed by the hydroxyproline assay. Because of the considerable range of values to be expected from this assay on skin pieces, resulting from the large dilution of the hydrolyzate necessary to secure readable colorimetric data and the consequent amplification of the analytical errors, interpretation of Table IV is somewhat difficult. However, it would seem safe to conclude that collagen purification is a function of the bating, since the overall summary of the longer times of bating and the use of enzymes does show a purer collagen than is shown by the short time bating samples and the water controls. Further, when the moisture content of the pieces is taken into account, the pieces have been purified by bating sufficiently to analyze as almost pure collagen by this procedure, while the pieces before bating contained up to 10 per cent of components not analyzing as water or collagen.

TABLE V

Collagen Solubilization by 60°C Water Extraction of Bated Skins

Enzymatic Preparation	Conc.	Bating Time 1	2	3	4½	6 hours
		Mg. Collagen 1G. Skin				
Water Control	——	275	300	——	——	367
Pancreatic Commercial bate (Oropon WN-4)	0.1	465	735	635	630	580
Microbial Bate (P 166)	0.4	456	695	655	620	500
Pancreatic Type	0.1	565	685	715	685	560
Tryptic Type	0.1	500	520	415	450	394
Crystalline Trypsin	0.1	380	595	495	520	500

Collagen alteration as a function of bating is shown in the data comprising Table V. These data were secured in an attempt to measure the presence of gelatinized collagen in the bated pieces. The procedure of extracting the ground skin squares for 1 hour at 140°F has been found in this laboratory to be able to separate gelatin and collagen when the former is dried onto native collagen. However, the data of Table V show that all of the enzyme preparations have altered the collagen permitting its extraction by water at 140°F; all of the enzyme treated pieces show significantly greater extraction of collagen, as indicated by the hydroxyproline assay, than is extracted from the water control.

Neuman and Tytell [7] have postulated that this alteration is due to adsorbed enzyme which hydrolyzes the collagen during the extraction period. However Gustavson [2] favors the interpretation that the collagen is modified so that it is more readily solubilized by the action of water alone. Our data are not sufficiently precise to permit positive conclusions in this regard. It may be noted, however, that the two longer bating periods yield spent bating liquors which contain an increased level of solubilized collagen. Further, the pieces from the longest bating period show a trend toward a lower collagen purity from the hydroxyproline assay values (Table IV). These observations would be consistent with an interpretation that the collagen is being modified with a removal of a hydroxyproline containing component. However, more precise evidence will be required before this can be accepted as an explanation of the sensitivity of bated skin pieces to hot water.

Summary

A microbiological bating preparation has been compared to a pancreatic bating material by the use of the Moore procedure and the procedure of McLaughlin and Wilson. These two procedures show that the two enzymes have similar bating action. It seems logical to compare them in actual tannery bating trials.

Use of the hydroxyproline assay procedure as an indicator of collagen has shown that bating removes relatively little collagen from limed skins, indicating that removal of denatured collagen from the skin does not play a significant role in bating. However, evidence is presented which indicates that bating alters the collagen, permitting its solubilization by the action of water at 140°F., perhaps by the removal of a hydroxyproline containing fraction from the collagen. However, more precise analytical data will have to be secured before this evidence can be validated.

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Bibliography

1. Anderson, H. J., *J. Soc. Leather Trades' Chemists*, **25,** 35 (1941). **29,** 209 (1945).
2. Gustavson, K. H., *J. Amer. Leather Chemists' Assoc.*, **44,** 392 (1949).
3. McLaughlin, George D., and Wilson, Harry R. *J. Amer. Leather Chemists' Assoc.*, **41,** 155 (1946).
4. Merrill, Henry B., Private Communication, 1951.
5. Moore, H. N., *J. Amer. Leather Chemists' Assoc.*, **44,** 326 (1949).
6. Neuman, R. E., and Logan, Milan, *A. J. Biol. Chem.*, **184,** 299 (1950).
7. Neuman, R. E. and Tytell, A. A., *Proc. Soc. Exptl. Biol. Med.* **73,** 409 (1950).

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Amide Nitrogen of Collagen and Hide Powder

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Abstract

The amide nitrogen of collagen, hide powder, and gelatin is shown to be 6.0, 3.8, and 1.9 milligrams per gram of protein. These values were obtained by determining the ammonia liberated by acid hydrolysis over an extended period and extrapolating back to zero time to get the amide nitrogen value.

The reaction involved in the hydrolysis of the amide bonds in collagen by 0.2 *N* hydrochloric acid at 100°C follows first order kinetics until almost 90 per cent of the reaction is complete and the specific reaction rate is calculated to be 30.4 x 10^{-5} sec^{-1}. An activation energy of 18,300 calories per mole was determined.

The rate of liberation of amide nitrogen from collagen is shown to be greater than from egg albumin. The catalytic effect of the sodium salts of certain mono and diabasic sulfonic and sulfuric acids, i. e., sodium lauryl sulfate, on the acid hydrolysis of amide groups is shown to be considerably greater with wool and egg albumin than with collagen.

The source of amide nitrogen in collagen is shown to be mainly asparagine rather than glutamine.

Introduction

As early as 1872 Nasse [1] observed that the nitrogen that gives rise to ammonia on hydrolysis of proteins, is bound differently in the molecule from the nitrogen found in the amino groups after hydrolysis. The estimation of this nitrogen, now usually referred to as amide nitrogen, has been the subject of much research. Many protein chemists have long considered that the ammonia produced on complete hydrolysis of proteins is in excess of that arising from acid amide residues, on account of the decomposition undergone by certain of the amino acid residues while still in peptide combination or

after their appearance as free amino acids. The determination of amide nitrogen is at present carried out by one of three methods: (a) an acid hydrolysis technique of Gordon et al [2]; (b) a somewhat similar hydrolysis method of Shore et al [3]; and (c) the alkaline hydrolysis procedure of Warner and Cannan [4] extensively used by Brand and his coworkers [5]. Although no amide nitrogen method was proposed by Steinhardt and Fugitt [6] they were able to show that certain anions very effectively catalyzed the liberation of the nitrogen from the amide groups of wool, while little effect on the peptide groups was detected.

The method of Gordon requires hydrolysis of the protein at 37°C with concentrated hydrochloric acid until the ammonia liberated reaches a substantially constant value. Rees [7] found this required 200 to 300 hours depending on the protein used. Tristram [8] observed that the alkaline hydrolysis method could readily yield high values with proteins containing hydroxy amino acids. The method suggested by Shore et al for estimation of amide nitrogen of egg albumin, was to hydrolize the protein for 6 to 10 hours at 100°C with 20 per cent hydrochloric acid, or to reflux the protein 3 to 5 hours with the same acid concentration. Provided the latter method is accurate, its convenience would recommend it. In this paper are presented some determinations of the amide nitrogen of collagen and two related products, hide powder and gelatin, by a method similar to that of Shore, and some data are given regarding the catalytic effect of several anions on hydrolysis of the amide groups of these same proteins by 0.2 *N* hydrochloric acid.

Materials and Methods

The collagen analyzed during these experiments was a highly purified grade prepared from steer corium by the method of Highberger [9]. The hide powder and gelatin were commercial products. With the exception of the lauryl sulfonate, which was a technical product, the reagents used in studying the catalytic effect of certain anions on amide nitrogen liberation were c.p. grade and were used as received without further purification. One hundred milliliters of the hydrolyzing acid heated to the desired temperature was added to a one gram sample of protein in a glass stoppered flask. Hydrolysis of the protein at temperatures greater than 100°C. was accomplished in an autoclave. Hydrolysis at other temperatures was carried out in an oven.

After the desired time had elapsed, the flask was cooled and the hydrolyzate was filtered through No. 41 Whatman filter paper. The filtrate was made weakly basic to phenolphthalein; sufficient dry calcium hydroxide was added for saturation and after addition of a few drops of capryl alcohol as an antifoamer, the ammonia was distilled under vacuum for ten minutes at 55°C. into 2 per cent boric acid containing a mixture of methyl red and methylene blue as an indicator. To recover liberated ammonia completely, it was found necessary to use a series of two boric acid traps and to reduce the pressure

just enough to obtain a small but steady flow of air through the capillary in the reaction vessel. Liberated ammonia was titrated with standard acid.

Results and Discussion

Shore, Wilson, and Stueck, in their paper on the amide nitrogen of ovalbumin, point out that the curve which relates formation of ammonia during acid hydrolysis to time is not that of a simple reaction. These authors state, "It appears to be the resultant of a rapid process complete in a few hours and a much slower reaction which continues indefinitely. It is generally assumed that the more rapid reaction consists in the hydrolysis of primary acid amide groups. The secondary evolution of ammonia is usually attributed to such reactions as may be comprehended in the term deamination."

Figure 1 and Figure 2 give the rates of ammonia formation obtained in the present study for collagen and hide powder. The proteins were hydro-

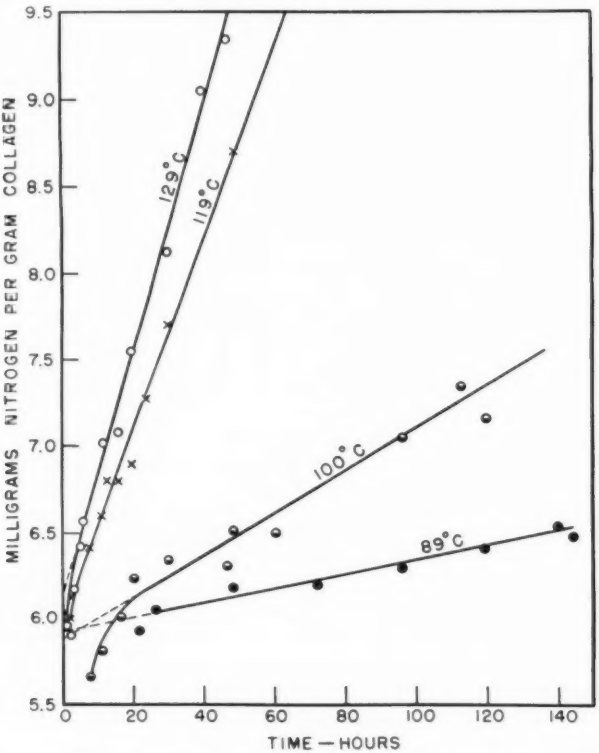

FIGURE 1.—Rates of evolution of nitrogen from collagen in 6 *N* hydrochloric acid.

lyzed with 6 *N* hydrochloric acid, except in the one instance when hide powder was hydrolyzed with a normal hydrochloric acid solution. From the straight line slopes in these figures the rates of nitrogen evolution are calculated to be 0.0061, 0.0049, 0.0011, and 0.0004 millequivalents per gram of collagen per hour at 129°, 119°, 100°, and 89°C. respectively. The corresponding values, for hide powder at 129°, 119°, and 100°C. are 0.0061, 0.0028, and 0.0010 millequivalents. The rate at 100°C. for both proteins is very near that of egg albumin (0.0014) as determined by Shore et al.

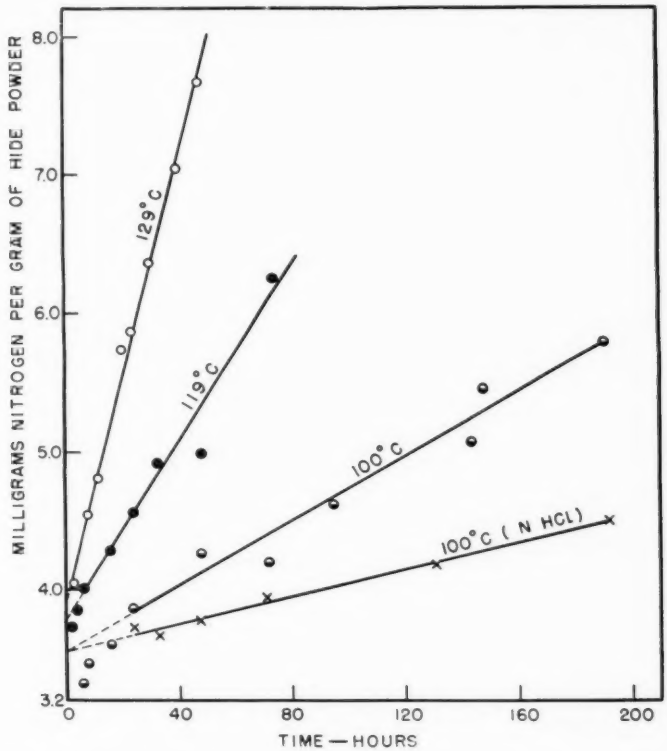

FIGURE 2.—Rates of evolution of nitrogen from hide powder in 6 *N* and *N* hydrochloric acid.

If both deamination and deamidation are involved in the early part of the ammonia liberation process, then extrapolation of the straight line representing the deamination rate should meet the ordinate at a value corresponding to the equivalents of amide nitrogen in the protein. From Figures 1 and 2,

it is evident that, in general, the extrapolated values decrease with a decrease in temperature. Shore et al believed this was due to the fact that deamination does not become established at its full rate until hydrolysis of the protein is far advanced and hydrolysis of amides nearly complete. These investigators found that complete solution of egg albumin did not occur until the curve of their deamination plot (similar to those in Figure 1) approached its straight line phase. This point was reached with egg albumin in 20 hours at 85°C. and in 10 hours at 100°C. In contrast to this, 95 per cent of the collagen was in solution at 100°C. in fifteen minutes.

Extrapolation of the straight lines representing the deamination rates in Figures 1 and 2 leads to the conclusion that the probable value for the amide nitrogen of collagen lies between 5.9 and 6.1 milligrams per gram and that for hide powder the value is 3.6 to 3.9 milligrams per gram. One is tempted to argue that the intercept values derived from the data at 129°C. are the

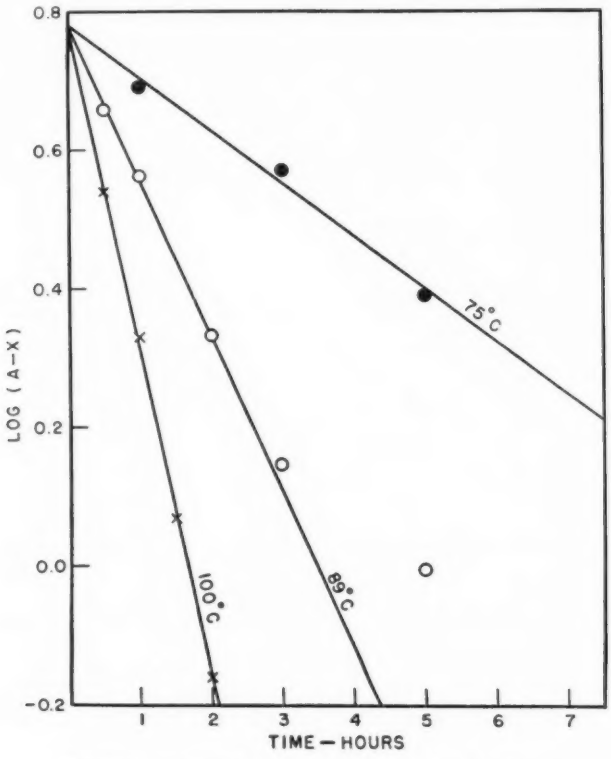

FIGURE 3.—First order plots of deamidation of collagen.

most accurate because in these instances the extrapolation is so small as to introduce a negligible error. It is doubtful however if such precision is justified and for that reason the median value has been used as the most probable value. For collagen and hide powder, this value is 6.0 and 3.8 milligrams per gram of protein. Extrapolation of the straight line representing the deamination rate of gelatin at 100°C. in 6 *N* hydrochloric acid gave a value of 1.9 milligrams per gram.

In Figures 3 and 4 data obtained from measurements of the initial phase of ammonia production from collagen and hide powder at 75°, 89°, and 100°C. are plotted in semi-log form. The ordinate is the logarithm of unreacted amide nitrogen per gram of protein where A is the initial concentration of amide nitrogen and x the amount reacted in time t. Values of 6.0 and 3.8 milligrams of nitrogen per gram were used for the value of A for collagen and hide powder, respectively. A 0.2 normal hydrochloric acid solution was the hydrolyzing agent used in these experiments.

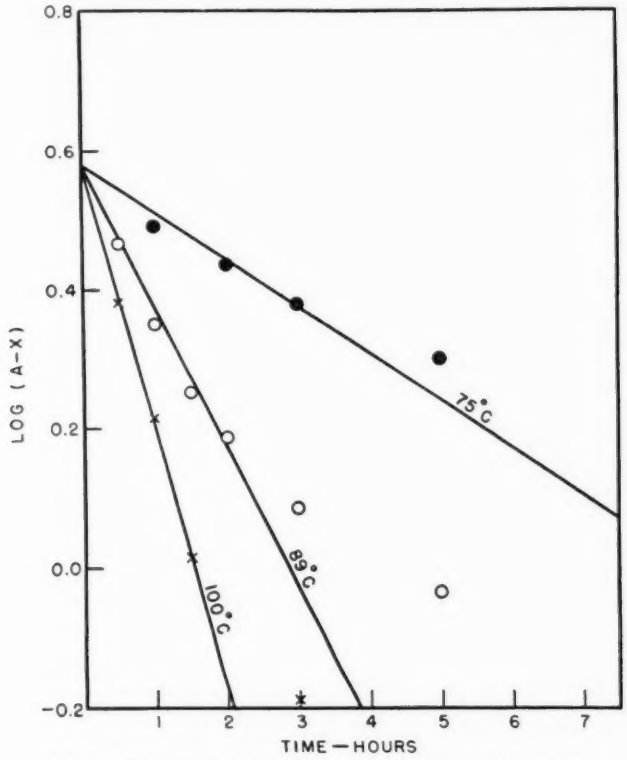

FIGURE 4.—First order plots of deamidation of hide powder.

From Figure 3 it is evident that the hydrolysis of the amide groups of collagen by 0.2 *N* hydrochloric acid follows first order kinetics until 90 per cent of the amide nitrogen has been liberated at 100°C. 80 per cent at 89°C. and 60 per cent at 75°C. The rate of evolution of ammonia from hide powder is similar to that of collagen in that the hydrolysis (Figure 4) follows first order kinetics until 70 per cent of the amide nitrogen has been liberated at 100°C 60 per cent at 89°C. and 35 per cent at 75°C.

To obtain specific reaction rates from the data in Figures 3 and 4 the slopes of the straight lines were multiplied by 2.303 in accordance with the equation for a first order reaction.

$$K = (2.303/t) \log (A/A-x)$$

where t is expressed in seconds and A and x are defined as before. The specific reaction rates at 75°, 89°, and 100°C. are 5.2, 14.4, and 30.4 x 10^{-5} sec^{-1}

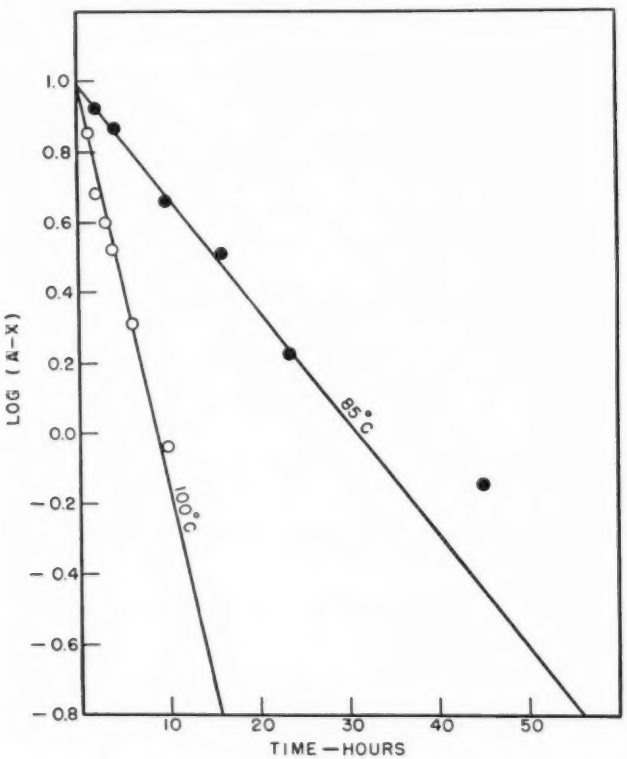

FIGURE 5.—First order plots of deamidation of egg albumin.

for collagen, and 4.4, 13.0, and 24.0 x 10^{-5} sec^{-1} for hide powder. The Arrhenius equation relating specific reaction rate and absolute temperature is

$$\log K = -E/(2.303RT) + C$$

in which K is the specific reaction rate, E is the activation energy, R the gas constant, and T the absolute temperature. From a plot of the logarithm of reaction rate versus the reciprocal of the absolute temperature, the activation energy for the hydrolysis of amide groups of collagen by 0.2 N hydrochloric acid was calculated to be 18,300 calories per mole.

In Figure 5 is shown a semi-log plot of the liberation of ammonia from egg albumin at 100°C. by 0.2 normal hydrochloric acid. This graph has been plotted from calculations made on the experimental data of Shore et al. There appear to be some significant differences in the liberation of ammonia from collagen and egg albumin. The hydrolysis of egg albumin follows first order kinetics for better than 10 hours at 100°C. and 25 hours at 85°C. In 10 hours at 100°C., 90 per cent of the amide groups of the egg albumin were hydrolyzed and in 25 hours at 85°C., 85 per cent had reacted. It is apparent that the rate of liberation of ammonia is greater for collagen than for egg albumin. The specific reaction rates at 85° and 100°C. calculated from

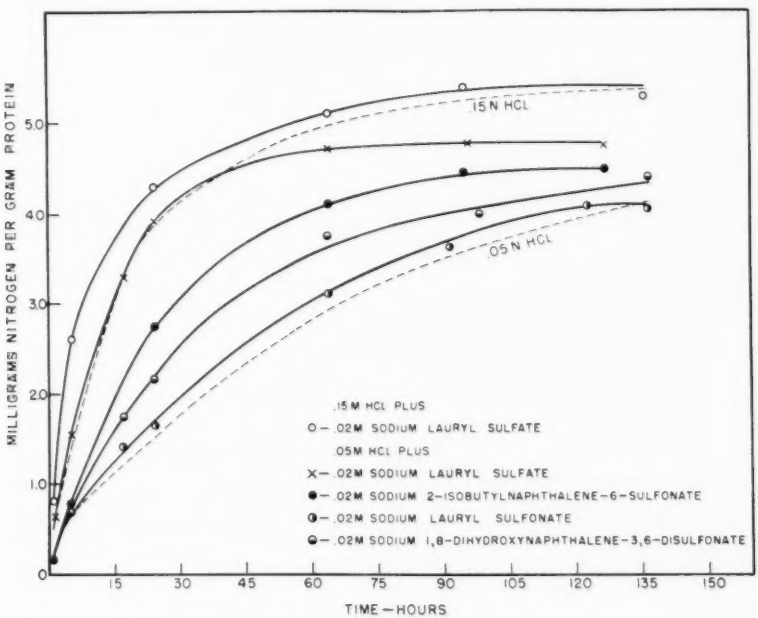

FIGURE 6.—Amide hydrolysis of collagen at 65°C as affected by certain anions.

the semi-log plot of Shore's data shown in Figure 5 are 2.01×10^{-5} and 7.34×10^{-5} sec^{-1}, respecctively.

Effect of Certain Anions on Amide Hydrolysis

The work of Steinhardt and Fugitt [6] in 1942 showed that hydrolysis of the amide groups of wool was very sensitive to certain catalytic agents, such as the sodium salts of certain mono and dibasic sulfonic and sulfuric acids. By keeping the concentration of these catalytic anions slightly below stoichiometric equivalence to the sum of the amino plus amide groups, the amide groups of the wool were rapidly hydrolyzed in dilute hydrochloric acid without extensive hydrolysis of peptide bonds.

Since this technique represents a different approach to the determination of amide nitrogen, it was thought worthwhile to investigate the effect of several such catalytic anions on the evolution of ammonia from the amide groups of collagen.

In Figure 6 the rate of hydrolysis of the amide groups of collagen by acid alone and by acid with several sulfates and sulfonates is compared. Steinhardt and Fugitt showed that anions of the type referred to in Figure 6 were catalytically effective only in dilute acid media and at relatively low temperatures. For this reason, hydrochloric acid strengths from 0.05 normal to 0.15

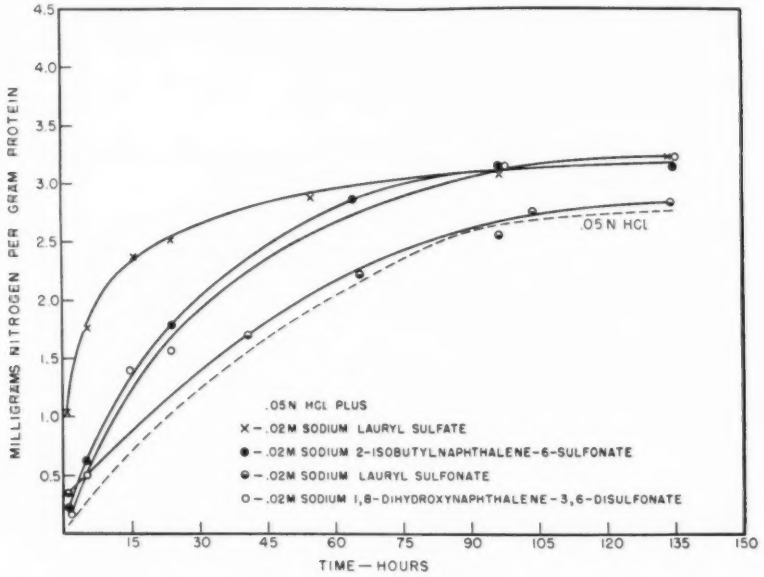

FIGURE 7.—Amide hydrolysis of hide powder at 65°C. as affected by certain anions.

normal were used in this phase of the investigation, and a temperature of 65°C. (or 75°C.) was maintained.

From Figure 6 it can be seen that each of the anions (added as the sodium salt to give a 0.02 M concentration) had some catalytic effect in a 0.05 *N* hydrochloric acid medium. In contrast to the maximum effectiveness of lauryl sulfate, the least effective was the lauryl sulfonate. The ammonia evolution appears to be catalyzed by lauryl sulfate until two-thirds of the amide nitrogen of the collagen has been liberated. The catalytic effects of the sodium isobutyl sulfonate and the dihydroxynaphthalene sulfonate are midway between the almost noneffective lauryl sulfonate and the most effective lauryl sulfate.

When the acidity of the medium is raised from 0.05 *N* HCl to 0.15 *N* HCl the catalytic effect of the lauryl sulfate is almost removed. This is in contrast to the work of Steinhardt on wool which showed that while the catalytic coefficient decreased by increasing the acidity from 0.05 *N* HCl to 0.15 *N* HCl it did not disappear.

In Figure 7 a plot is shown of the ammonia liberation from hide powder in 0.05 *N* hydrochloric acid at 65°C. with and without the catalytic anions. The data are very similar to those obtained with collagen in that lauryl sulfate was most effective and lauryl sulfonate least effective with the catalytic activity of the other anions falling in between.

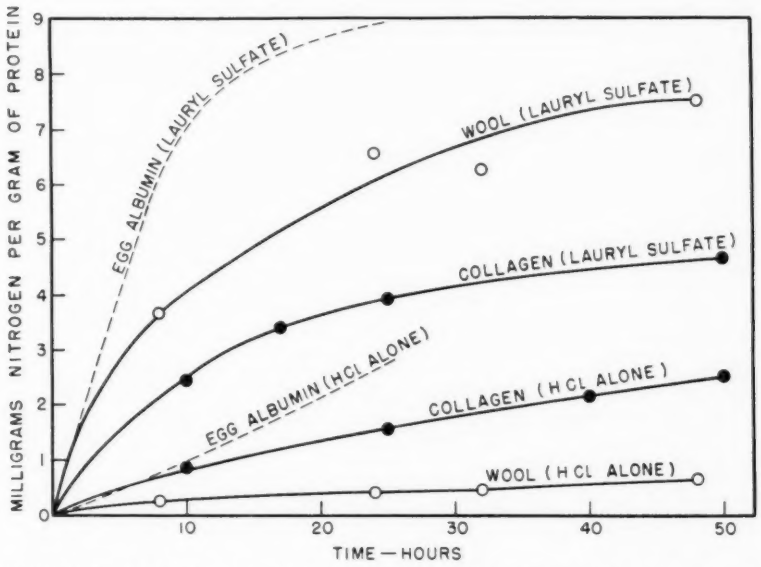

FIGURE 8.—Catalytic effect of lauryl sulfate on amide hydrolysis of egg albumin, wool and collagen at 65°C.

In order to make a fair comparison of the catalytic effect of these anions on the amide hydrolysis of wool and collagen, the rate of evolution of ammonia from wool in 0.05 *N* hydrochloric acid at 65°C. was determined with and without lauryl sulfate (0.02 M concentration used). These data are plotted in Figure 8 along with the data obtained by Steinhardt on egg albumin under similar conditions. From the data plotted it appears that the lauryl sulfate is much more effective in catalyzing the amide nitrogen evolution of either wool or egg albumin than of collagen.

The data o Figure 9 illustrate the effect of a ten-degree increase in temperature on the catalytic activity. While the catalytic activity of the lauryl sulfate is still very pronounced on wool, it has been almost completely eliminated on collagen by this slight increase in temperature. This result is presumably due to the relatively high percentage of amide hydrolysis occurring in acid alone.

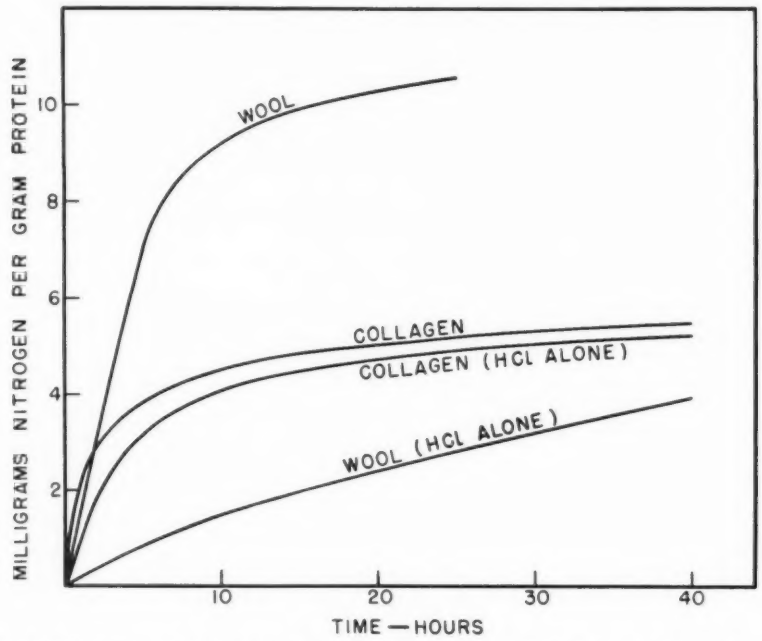

FIGURE 9.—Amide hydrolysis of wool and collagen at 75°C. with and without lauryl sulfate.

Asparagine, Glutamine Ratio in Collagen

According to the literature the source of the amide nitrogen of collagen is in the asparagine and glutamine residues. However, there has been no evi-

dence to indicate the extent to which either aspartic or glutamic acid may occur in collagen as amides. Vickery et al [10] showed that hydrolysis for three hours at 100°C. in *N* sulfuric acid would liberate all the amide nitrogen of asparagine and of glutamine. It was also shown that if the hydrolysis is carried out at pH 6.5 using a phosphate-borax buffer to maintain the pH, practically complete hydrolysis of glutamine is accomplished with almost no hydrolysis of the asparagine.

Experiments with the glutamine and asparagine products of Eastman Kodak showed that only 4 per cent of the asparagine but 92 per cent of the glutamine was hydrolyzed by a phosphate buffer (pH 6.5) in two hours at 100°C. Prolonged heating did not increase the glutamine hydrolysis.

TABLE I

Influence of Acidity on Liberation of Amide Nitrogen from Collagen and Hide Powder

Hydrolyzing Agent	Amide N per gram of protein	
	Collagen (mg)	Hide Powder (mg)
Sulfuric Acid	5.8	3.4
Phosphate Buffer	1.2	0.6

In Table I are shown the results of these same hydrolysis conditions on collagen and hide powder.

If one assumes that the glutamine and asparagine residues of a protein liberate nitrogen by these hydrolysis methods as readily as do free glutamine and asparagine molecules, then the data in Table I indicate that the amide nitrogen source in collagen and hide powder is mainly asparagine. The asparagine:glutamine ratio in these two materials is calculated from Table 1 to be four to one.

Routine Determination of Amide Nitrogen in Collagen

From the data in Figures 1 and 2 it is evident that ammonia equivalent to the nitrogen of the amide groups of collagen and hide powder was liberated in an hour at 129°C. by 6 *N* hydrochloric acid. The precision of such a determination using an autoclave to obtain the desired temperature does not recommend it for a routine analysis. An equivalent amount of ammonia was liberated by the same acid concentration in 16 hours at 100°C. The convenience of this overnight procedure using an oven to obtain the desired temperature is readily apparent.

To liberate the ammonia from the hydrolyzate, it is suggested that either magnesium oxide or calcium hydroxide be added to the neutralized hydrolyzate to obtain the desired basicity and that the vacuum distillation be carried

out at 55°C. Care must be taken during neutralization of the hydrolyzate to keep the temperature from rising excessively. It is recommended that two traps containing two per cent boric acid be used to absorb evolved ammonia and that the pressure be reduced just enough to maintain uniform boiling in the distilling flask. Titration of absorbed ammonia may be accomplished in the ordinary manner with dilute hydrochloric acid.

Conclusions

The amide nitrogen value of a purified collagen, of hide powder, and of gelatin has been found to be 6.0, 3.8, and 1.9 milligrams per gram of protein. The reaction involved in the hydrolysis of amide bonds in collagen at 100°C. follows first order kinetics until almost 90 per cent of the reaction is complete. The specific reaction rate for the evolution of amide nitrogen from collagen at 100°C. by 0.2 *N* hydrochloric acid was calculated to be 30.4×10^{-5} sec^{-1}. An activation energy of 18,300 calories per mole was determined for this reaction.

The rate of liberation of amide nitrogen from collagen is shown to be much greater than from the reported rate for egg albumin. The catalytic effect on this reaction by the sodium salts of certain mono and dibasic sulfonic and sulfuric acids, i. e., sodium lauryl sulfate, is shown to be considerably greater than the effects reported for wool and egg albumin.

The source of amide nitrogen in collagen is shown to be mainly asparagine rather than glutamine.

References

1. Nasse, O., *Arch. ges. Physiol.*, **6**, 589 (1872).
2. Gordon, A., Martin, A., and Synge, R., *Biochem. J.*, **35**, 1369 (1941).
3. Shore, A., Wilson, H., and Stueck, G., *J. Biol. Chem.*, **112**, 407 (1935).
4. Warner, R., and Cannan, K., *J. Biol. Chem.*, **142**, 725 (1942).
5. Brand, E., and Kossell, B., *J. Biol. Chem.*, **145**, 365 (1942).
6. Steinhardt, J., and Fugitt, C., *J. Research NBS*, **29**, 315 (1942) R. P. 1503.
7. Rees, M., *Biochem. J.*, **40**, 632 (1946).
8. Tristam, G., Advances in Protein Chemistry, Vol. 5, p. 88, Academic Press, New York, N. Y. (1949).
9. Highberger, J., *J. Am. Leather Chem. Assoc.*, **31**, 93 (1936).
10. Vickery, H., Pucher, G., Clark, H., Chibnall, A., and Westall, R., *Biochem. J.*, **29**, 2710 (1935).

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The Over-All Basicity of Chrome Tanned Leather*

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In a recent paper [1] from the Lehigh Laboratories, the neutralization of chrome tanned leather prior to coloring, was discussed in some detail. For these studies the reduction of acidity, layer-wise, was followed by using methods developed twenty or more years ago by Gustavson [2] and Merrill [3]. The basicity of the leathers was determined by the standard ALCA method, originated by Thomas [4] in 1920. The protein bound acidity diffusion method leaves much to be desired as pointed out by McLaughlin and Theis [5] but in this year of 1953, no investigator has originated an analytical method which will sharply and definitely differentiate the protein and chromium bound acid.

The present official ALCA method of determining the total sulfuric acidity of chrome tanned leathers has just recently been investigated by a committee of the Association. This committee came to the same conclusion as that of Theis and Meerbott [6] in 1942, who advocated the use of dilute ammonia in place of sodium dihydrogen phosphate for removing the acid anions associated with the protein and chromium. These investigators pointed out at that time that the ammonium hydroxide extraction method gave quite excellent check results, that it was simpler to use, lends itself more readily relative to differentiating the various anions, and was not subject to the same co-precipitation errors as was the case of the phosphate extraction method. Over the past 10 years, this laboratory has used the ammonia replacement method, as outlined by Theis and Meerbott, for data necessitating the determination of other anions than those of sulfuric acid.

Since the analytical determination of sulfates has been under critical investigation by an Association committee, we have investigated the errors involved in both the phosphate and ammonia displacement methods. We found large errors in the phosphate method—some 11 per cent if the amount of hydrochloric acid specified by the ALCA method is used and but small and insignificant errors if the ammonia displacement method is employed. These data are shown in Figure 1. Such data account only for the sulfuric acid held either with the collagen or the chromium atom and are not sufficient for calculating the true over-all acidity of chrome tanned leathers.

When chrome tanned leather, in the "blue" (prior to coloring, etc.) is analyzed for its various acidities, different conditions obtain than those for finished leather and therefore it appears to us that these different states must

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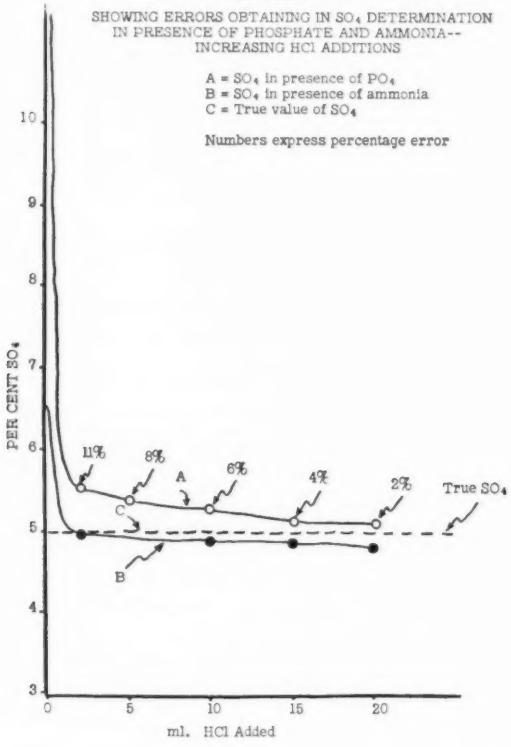
FIGURE 1

SHOWING ERRORS OBTAINING IN SO_4 DETERMINATION IN PRESENCE OF PHOSPHATE AND AMMONIA-- INCREASING HCl ADDITIONS

A = SO_4 in presence of PO_4
B = SO_4 in presence of ammonia
C = True value of SO_4

Numbers express percentage error



be taken into account if correct or nearly correct answers are desired. Leather in the "blue" must of necessity contain the following cations and anions—Na^+, H^+, $SO_4^=$, Cl^-, HSO_4^-. The present ALCA method takes into account the HSO_4^- and $SO_4^=$ ion, using the premise that only the $SO_4^=$ ion is important. To our way of thinking, it is necessary to take fully into account the Cl^- and other anions associated with the collagen and the chromium atom. This last statement is of real importance.

With the exception of the determination of the acidity of the water extract, applicable for the removal of any easily diffusible acid anoin, there have been only insignificant changes in the method of determining sulfates in leather since Thomas first devised the method in 1920. Since the method has largely been used for finished leathers and not for chrome leathers containing real amounts of soluble salts—NaCl, Na_2SO_4, etc. It looked to us that the method should be investigated in real detail so that it could serve a more useful purpose for leathers in any state of the process.

The ALCA method was used for calculating the so-called basicity of the leather by subtracting the acidity percentage from 100. If other anions than sulfato groups are present, and are not taken into account, the acidity figure for the leather is not correct.

TABLE I

A—Effect of Weight of Sample

		1	2	3	4	5	6	7	8	9	10
Weight Sample Grams	Hours Extraction	SO_4 Extraction by NH_3	SO_4 Extraction by H_2O	Cl Extraction by NH_3	Cl Extraction by H_2O	Titratable Acidity Water Extract	Acid SO_4 1–2	Acid Cl 3–4	Total Acid 5+6+7	OH Assoc. With Cr by Dif.	OH** Assoc. With Cr by Anal.
0.5	2	1.03	0.49	1.77	1.68	0.28	0.54	0.09	0.91	0.14	0.17
1.0	2	1.05	0.48	1.76	1.63	0.22	0.57	0.13	0.92	0.13	0.17
1.5	2	1.06	0.49	1.73	1.60	0.19	0.57	0.13	0.89	0.16	0.17
2.0	2	1.07	0.49	1.75	1.60	0.18	0.58	0.15	0.91	0.14	0.17
B—Effect of Time Period of Extraction											
1.0	0.5	1.07	0.46	1.78	1.67	0.23	0.61	0.11	0.95	0.10	0.17
1.0	1.0	1.09	0.48	1.76	1.66	0.24	0.61	0.11	0.96	0.09	0.17
1.0	1.5	1.09	1.47	1.79	1.67	0.24	0.62	0.12	0.98	0.07	0.17
1.0	2.0	1.08	0.48	1.76	1.64	0.22	0.60	0.12	0.94	0.11	0.17
1.0	3.0	1.07	0.52	1.77	1.65	0.23	0.55	0.12	0.90	0.15	0.17
1.0	4.0	1.08	0.52	1.81	1.65	0.23	0.56	0.16	0.95	0.10	0.17
1.0	5.0	1.09	0.53	1.80	1.65	0.22	0.56	0.15	0.93	0.12	0.17
1.0	6.0	1.08	0.55	1.78	1.64	0.23	0.53	0.14	0.90	0.15	0.17

*All values expressed in milli-equivalents per one gram leather sample.
**Lehigh method of determining over-all basicity to be discussed later.

Further study of the ALCA method for determining sulfato and other anionic groups was made along various lines. Since most chrome tanned leathers are pickled and tanned in the presence of sodium chloride, sodium sulfate, hydrochloric and sulfuric acids, it was decided to study the neutral and acid chloride groups present in the leather as well as the neutral and acid sulfate groups. Table I–A gives data relative to all of these components, the only variable being the weight of sample taken for extraction. This sample weight varied from 0.5 to 2.0 grams. Table I–B gives similar data but, in this case, one gram samples were used and the variable was the time of extraction for both the water and ammonia extraction periods. Before analyzing these data, it should be pointed out that the type of leather used for these various analyses was chrome tanned using a sugar reduced chrome liquor which liquor was made by using the minimum amount of sugar necessary for the reduction of the acid dichromate. Therefore, this particular chrome leather contained sodium chloride, sodium sulfate, acid sulfate, and acid chloride along with the hydroxyl ions associated with the chromium atom. This leather contained

no masking salts and therefore organic anions are at a minimum. Such being the case, the total acid sulfate together with the acid chloride and the titratable acidity of the water extract should add up to the total acid anions present in the chrome tanned leather and the difference from one hundred should be a measure of the hydroxyl groups associated with that leather. In other words, these hydroxyl groups obtained by difference should be a measure of the over-all basicity of that particular leather. That this is the case for this leather is shown in Table 1.

Analysis of data shown in Table 1 indicates the following basic facts.

1. If the premise that the difference between the total sulfates extracted by means of ammonia solution and the sulfates extracted by water alone is correct then it is necessary to extract the chlorides in the same manner as that of the sulfates. In other words, acid chlorides as well as acid sulfates are associated with the protein and the chromium atom. This fact can readily be seen by a study of Table 1.

2. Further, to obtain the correct values for anions associated with the protein and the chromium, it is necessary to titrate the water extracted sample. The total of acid sulfates, acid chlorides and the titratable acidity for this particular leather gives the total anions associated with the protein and the chromium atom, and therefore this total subtracted from the milliequivalents of chromium per gram leather sample gives the value for the hydroxyl ions associated with the chromium.

3. If the acid sulfates, acid chlorides and titratable acidity are determined the amount of sample and the time of extraction, either in water or ammonia, are not critical as can readily be seen from Table 1.

4. The facts pointed out by paragraphs 1, 2, and 3 are only applicable to leathers in the "blue" and for leathers tanned in a chrome liquor containing no appreciable amounts of masking or stabilizing salts. If stabilizing salts are present during the tannage, it is then necessary to determine the other anions such as the organic ones which are associated with the protein and with the chromic atom.

5. For leathers in the crust or finished state, the probabilities are that no real amounts of acid chloride will be present but on the other hand, anions belonging to any syntan groups, the vegetable tannin groups or mordant groups, will play a predominating role. In some cases these groups displace almost entirely the sulfato groups.

Column 9 of Table 1 shows the difference value between milliquivalents chromium and the total milliquivalents acid anions determined for this particular leather. It is very interesting to compare column 9 with column 10 which shows the OH values for this particular leather determined by a new analytical method. The new method, which will be described in detail later in this report, simplifies the entire procedure, since it is not necessary to determine the acid anions present in the leather. Determining all the acid anions present in the leather can be a very tedious and time consuming

process, and therefore the new method was developed but, in order to present the new method, it appeared necessary to us that we should first show that if we could determine with reasonable accuracy the acid anions present and take this total and subtract it from the milliequivalents of chromium and thus obtain a value approximately equal to that obtained by the new method, it would strengthen the principles upon which the new method is based.

The analytical methods used for obtaining the data in Table 1 are approximately the same as those advocated by the Mineral Tannage Committee of the ALCA for sulfates in leather with the exceptions, (1) 250 ml. beakers were used in place of volumetric flasks, and (2) the same sample after water extraction is used for the ammonia extraction. Identical procedure as far as extraction is concerned is used for the soluble and total chlorides of the leather. Due to a small amount of protein being dissolved, gravimetric precipitation of the silver chloride rather than the volumetric method was employed.

Even for chrome tanned leather in the "blue" it is necessary to determine the acid chloride bound if the true over-all basicity of the leather should be desired. It is not sufficient to determine only the acid sulfate bound by the protein and chromium atom. The writers feel that if the premise for the determination of the sulfate bound to the protein and chromium atom is correct, then the modified method for acid chloride is also correct. Further, since the addition of the acid sulfate, the acid chloride and the titratable acidity subtracted from the milliequivalents of chromium gives approximately the same results as obtained by the new method, it is felt that the principles suggested above are correct.

If we take data from Table I-A (1-gram sample and 2-hour extraction time) we find that the basicity as calculated from the acid sulfate to be 45.72 per cent. If we use data for the acid sulfate plus the titratable acidity, we find the basicity to be 24.76 and if we take data for the acid sulfate, titratable acidity and acid chloride, we then find the basicity to be 12.38 per cent. Taking data from Table I-B for 1-gram sample and 2-hour extraction time, we find the basicities under the same conditions to be 42.86 per cent, 21.90 per cent and 10.47 per cent. These data indicate that we cannot merely use the sulfato and titratable acidity as the total acidities of chrome tanned leather in the "blue" but we must use the complete acidities and so take into account the acid chloride present. Thus we note that if we take into account the acid sulfate, the titratable acidity and the acid chloride, we arrive at a figure for over-all basicity of approximately 11 to 12 per cent. Comparing this figure with the over-all basicity as obtained by the newly developed method, namely, 16.19 per cent it would seem that the data compared most favorably.

It will presently be shown that if the tannage is made in the presence of stabilizing salts, the over-all basicity as calculated from the acid sulfate, the acid chloride and titratable acidity does not approximate the over-all basicity as obtained by the new method because in order to so do, we must

know the amounts of the organic anions present. This discrepency will be indicated later on in this paper.

In 1952 Thorstensen and Theis[7] introduced a method for the factual determination of the over-all basicity of basic chrome liquors. The actual method was not new in principle in that the reaction employed dates back to the year 1925 at which time Fiegl and Kraus[8] discussed its application to aluminum salts:

$$Al(OH)\,SO_4 + 3K_2C_2O_4 \longrightarrow K_3\,[Al(C_2O_4)_3] + KOH + K_2SO_4$$

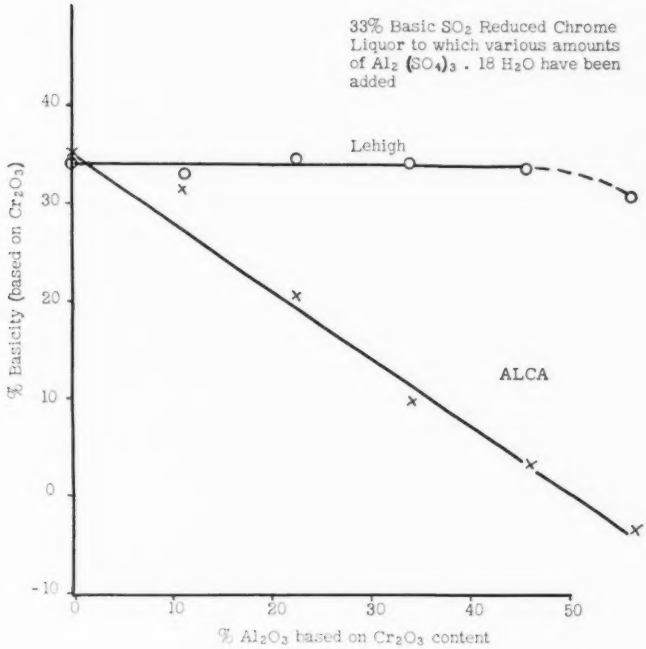
The replacement of sulfato and hydroxyl groups is practically complete for basic aluminum salts but such is not the case for the basic chromium salts. Blaedel and Panos[9] in 1950 investigated several methods for determining the acidity and basicity of aluminum salts. These investigators discuss the advantages of potassium oxalate over potassium flouride and other complexing agents in the determination of these factors. Their method, however, applied only to aluminum salts.

Thorstensen and Theis, independently worked out a similar method to that used by Blaedel and Panos but in this case applied it to basic chromium sulfate. The actual method used sodium oxalate and sulfuric acid and was based on the previous studies made by Theis and Thorstensen[10] and by Serfass, Theis, and Clark.[11] It had been demonstrated in 1946 and 1947 that oxalic acid penetrates and replaces other anions in the chromium complex very easily and for all intents and practical purposes quantitatively, converting the basic chromium salt to a "trioxalato" chromate. Serfass, Theis, and Clark utilized this principle in developing a rapid colorimetric method for determining chromium in various chrome liquors. The reaction postulated by Thorstensen and Theis was:

$$Cr(OH)SO_4 + 3Na_2C_2O_4 + H_2SO_4 \longrightarrow Na_3[Cr(C_2O_4)_3] + 1.5\,Na_2SO_4 + 0.5H_2SO_4$$

Thus the principle of the method rests on a postulation that the addition of sodium oxalate and a known amount of sulfuric acid to a basic chromium salt results in the production of a mole of sodium hydroxide (with the subsequent production of stable sodium trioxalato chromiate) which is immediately neutralized by the acid present. The acid is necessary for the chemical reaction to go to completion. The method has been described and discussed previously in *This Journal*. It should be pointed out that Ueberbacker and Droscher[12] in 1939 applied essentially the same principle as outlined by Thorstensen and Theis but in their case excess oxalic acid was added to the basic chromium salt solution and the excess oxalic and trioxalato chromic acid titrated with alkali. This method as given by these workers is applicable to simple chrome liquors but not those containing appreciable aluminum salts as will be explained in the following paragraphs.

FIGURE 2
COMPARISON OF LEHIGH AND ALCA BASICITIES
OF CHROME LIQUORS CONTAINING
ALUMINUM SALTS



The present authors found that the method as presented previously was not applicable to chrome liquors containing goodly quantities of aluminum salts, mainly due to the fact that sodium oxalate was not sufficiently soluble to give the necessary complexing effect with all of the chromium and aluminum ions present. The method was therefore modified and potassium oxalate specified because of its much greater solubility. Using the latest modification of the method as applied to chromium—aluminum liquors, Figure 2 results. From these data it can readily be seen that any reasonable amount of added aluminum salt will not affect the method as it relates to the true basicity (or acidity) of the original basic chrome liquor. It should be pointed out, however, that if the aluminum salt should be acidic or basic in character, the over-all basicity of the entire system will be affected to the degree of the acidity or basicity of the aluminum salt added.

In an attempt to apply this method to the determination of the over-all basicity of a chrome tanned leather, however, it was found that the acid hydrolysis of the hide substance introduced an error which varied with the

amount of acid present, the time of reflux, and the amount of hide substance present. An attempt to buffer the acid medium with sodium acetate produced results which were much less in error and for which the error could be calculated under specified conditions. However, the use of sodium acetate decreased the sensitivity of the method and required very careful analytical technique to obtain reproducible results.

Since potassium oxalate has a much greater solubility than sodium oxalate it was tried at higher concentration than was possible with the sodium oxalate and it was found that this reagent acted both as a buffer to prevent the hydrolysis of the hide powder and as a complexing agent for the chromium. A careful study was made, therefore to determine the conditions for the method using potassium oxalate. The hide powder used in these tests was specially prepared collagen which had been lightly limed and therefore, although it had a pH of 6.8, contained about 0.20 meq. of carbonate per 2.00 grams. Since in the method for basicity any CO_2 present is driven off, carbonate appears by analysis to be the same as OH ion. An analysis of the hide powder by the KI-KIO_3 method showed that it contained 0.185 meq. OH per 2.00 gram sample. A stock chrome liquor was made up to contain 3.81 meq. of chromium per 10 ml. and this liquor was tested for the effect of the various variables.

The results of the investigation indicate that above 25 meq. potassium oxalate both chromium and hide substance are stablized; that a reflux time of 1 hour is adequate to complete the reaction; and that from 2.5 to 7.5 meq. of acid are necessary.

The presence of aluminum in a chrome liquor caused incorrect values using the original sodium oxalate basicity method and therefore the effect of aluminum was redetermined using a large quantity of potassium oxalate. It was apparent that potassium oxalate may be used to stabilize aluminum as well as chromium provided an end-point pH 7.5 is chosen for the titration. Using the pH 7.5 end-point and a solution containing 2 meq. of aluminum, the effect of the concentration of potassium oxalate was measured. It was found that the results were correct down to 100 meq. of oxalate and that the error using 50 meq. of oxalate was less than 0.03 meq. of OH per 2 meq. of aluminum. Since aluminum is often encountered in tannery liquors, the final method selected is one which will allow for both aluminum and chromium in either liquor or for chrome tanned leather.

On the basis of the above data the following method is recommended for determining the over-all basicity of chrome liquors and chrome leathers either with or without aluminum present:

Sample:

(a) chrome liquor sample containing between 1.5 and 4.0 meq. Cr (.04 – .100 gms. Cr_2O_3)

(b) ground leather sample containing between 1.5 and 4.0 meq. Cr (.04 – .100 gms. Cr_2O_3)

Reagents:

(a) potassium oxalate stock solution (184 gms. C.P. $K_2C_2O_4.H_2O$ per liter)
(b) accurately standardized H_2SO_4 solution (about 0.5 *N*)
(c) sodium hydroxide solution approximately 0.25 *N*
(d) neutral anti-foaming agent (2 ethyl hexanol)

METHOD:

Put sample in 500 ml. Erlenmeyer flask, pipette in 15 ml. of 0.5 *N* H_2SO_4, add 25 ml. of potassium oxalate stock solution from graduate, add about 2 ml. of anti-foaming agent, add few glass beads and make up to about 100 ml. with water.

Boil under reflux (rubber stoppers, water condensers) for 1 hour. Cool, rinse down condenser, remove flask and rinse down stopper.

Titrate sample with 0.25 *N* NaOH at room temperature using pH meter for indicator (standardize meter against pH 7 buffer) to pH 7.5 end-point. Record ml. NaOH for sample and blank.

Calculations:

$$\% \text{ Basicity} = \frac{\text{ml } H_2SO_4 \times N H_2SO_4 - \text{ml NaOH (sample)} \times {}^*N \text{ NaOH}}{\frac{\text{gms } Cr_2O_3 \text{ (sample)}}{.02534}}$$

$$^*N \text{ NaOH} = \frac{\text{ml } H_2SO_4 \times N\ H_2SO_4}{\text{ml NaOH (blank)}}$$

TABLE II

Showing Basicities of Leather in the Finished State

	Grain	Corium
pH	3.35	3.50
Per cent H. S.	66.57	78.50
Meq./gm neutral SO_4	0.32	0.22
Meq./gm neutral Cl	0.11	0.03
Meq. acid SO_4	0.44	0.68
Meq. acid Cl	0.02	0.01
Meq. titratable acid	0.21	0.17
Meq. total acid 5+6+7	0.67	0.86
Meq. Cr_2O_3	1.63	1.50
Meq. OH by diff. 9–8	0.96	0.64
Meq. OH by Lehigh method	0.528	0.417
Meq. acid not accounted for 10–11	0.432	0.223
Total acid basicity 10/9	58.90	42.67
Lehigh Basicity 11/9	32.39	27.80
ALCA basicity $100 - \frac{5+7}{9}$	60.12	43.33

The data given in Figures 3 and 4 show complete values for leather in the "blue" previous to any washing effect—that is the leather contains all of the salts present in the leather after the tannage. All of the data thus given are in milliequivalents per gram of leather, thus the acidities or basicities can be readily calculated. Those data given in Figure 3 are for a non-formato-chrome tannage while those shown in Figure 4 are for a formato-chrome tannage. These data show the amounts of neutral salt present (both chlorides and sulfates), the acid sulfates, the acid chlorides, the titratable acids and the acids not accounted for. Thus from these data the standard ALCA leather basicity can be calculated as well as the Lehigh basicity figure. The data given in Figures 3 and 4 are self explanatory in that it can be seen that all acid anions must be taken into account if the true over-all basicity figure for leather is important.

For leather in the "crust" or "finished" state, the *real* over-all basicity figure differs drastically from the ALCA sulfato basicity value—usually the

FIGURE 3
SHOWING BASICITIES OF PRODUCTION LEATHER
(Non-Formato Chrome Tannage)

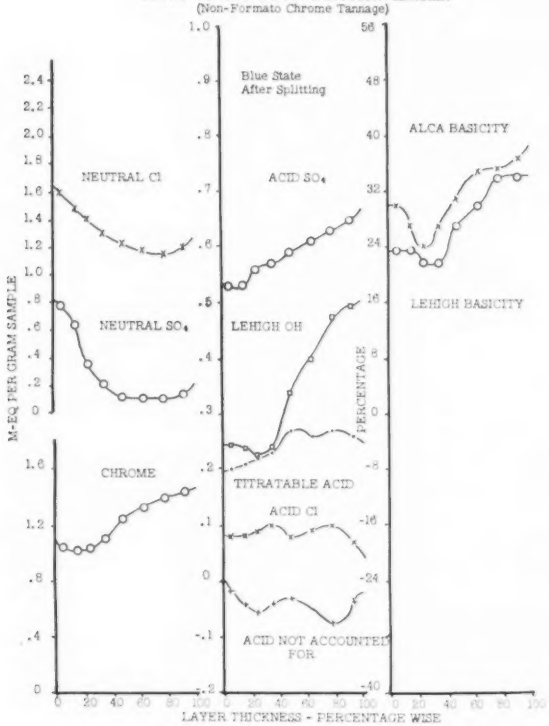
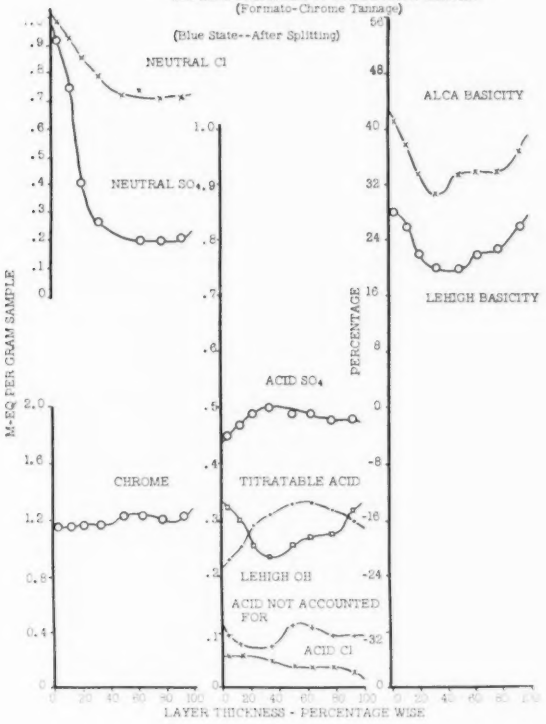
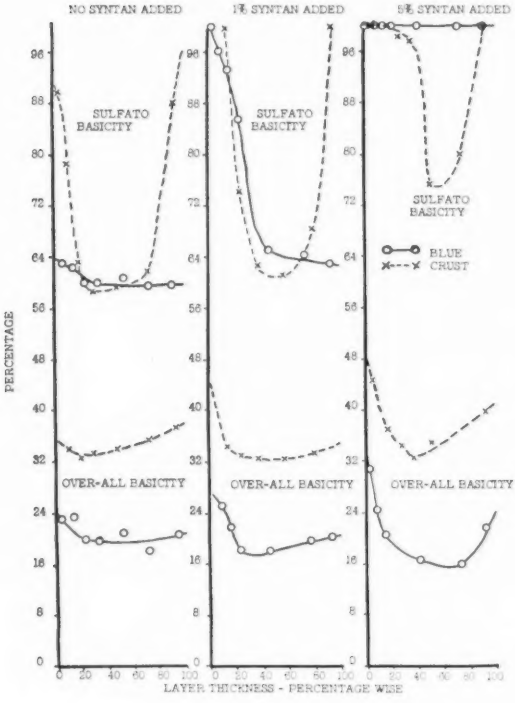


FIGURE 4
SHOWING BASICITIES OF PRODUCTION LEATHER
(Formato-Chrome Tannage)



"finished" leather is the one analyzed in the tanning. For leather that has been finished, the true basicity figure can not be determined because of the various anions that have been introduced by neutralization, mordanting, coloring, and finishing. Usually we find that many sulfato groups have been replaced by anions from naphthalenic syntans, dyes, mordants, vegetable tannins, and other agents used in the entire finishing cycle. Table 2 gives complete data taken from finished calf leather—for grain layer and for the leather with the grain removed. A study of these data indicates strongly that the Lehigh Basicity Method gives a lower value than does the ALCA Method. This is due, of course, to the replacement of sulfato groups by the mordant, dye, etc. anions—thus decreasing the sulfato acidity. This is shown in item 12, the milliequivalents of acid not accounted for. Therefore, the Lehigh Basicity Method, the present writers believe, gives a more realistic value and its use believed justified.

FIGURE 5
SHOWING SULFATO AND LEHIGH BASICITY DATA -
FORMATO-CHROME TANNAGE - SYNTAN ADDITIONS

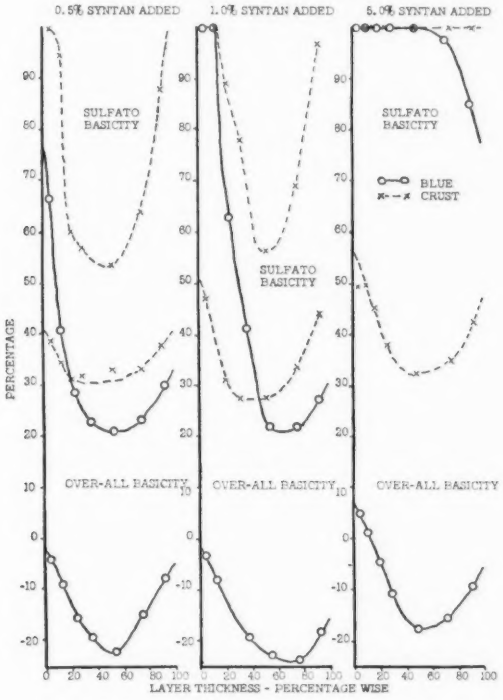


Figures 5 and 6 give data relative to the over-all basicity of leather in the "blue" and in the "finished" condition. Figure 5 shows the data for a formato-chrome tanned leather while Figure 6 shows that for a non-formato-chrome tannage. For the leather in the "blue", sampling occured just after splitting and shaving and thus the leather contained all of the neutral salts and acids such as obtained during the actual tannage. The leather had not been washed at the time of sampling. Thus the over-all basicity as determined by the Lehigh Method should and does indicate a real difference from the sulfato basicity. For the formato-chrome tanned leather the basicity figures are all positive in nature but not so for the non-formato-chrome tanned leather, as can be seen from the data of Figure 6.

As pointed out earlier in this paper, real and positive differences should exist between basicity figures obtained by the standard ALCA and the Lehigh method for finished leathers. These particular differences are shown in

a realistic manner in Figures 5 and 6 for finished leather. Figure 5 (data for no syntan added) shows particularly the effects of neutralizing prior to coloring and fat-liquoring, mordanting and coloring. The present writers believe that the Lehigh Method gives the approximate true basicity value. Certainly the sulfato basicity figure does not represent the over-all picture and represents just exactly the "sulfato" picture. The drastic differences obtaining can readily be seen by comparing the "sulfato" and Lehigh method, differences as shown in Figures 5 and 6 for 5 per cent syntan additions. For

FIGURE 6
SHOWING SULFATO AND LEHIGH BASICITY DATA -
NON-FORMATO-CHROME TANNAGE - SYNTAN ADDITIONS



leather in the "blue", the large amount of neutral naphthalenic syntan has almost in entirety replaced the sulfato groups. For leather in the "crust" the sulfato groups have increased to a small degree by the "chrome retannage" used.

Summary

A method has been developed for the determination of the over-all basicity of both chrome liquors and chrome tanned leathers. The method is applicable to liquor or leather containing iron or aluminum salts.

The principle of the method is an old one and is based on the rapid complexing activity of oxalic acid.

The data given in this paper, the writers believe, show rather conclusively the validity of the Lehigh method.

The method described has been used in this laboratory for better than a year with excellent results. It is not complicated and, in general, ordinary laboratory equipment can be used. The method has been used as a research tool in the study of the neutralizing reaction and these data will be shown in a series of papers about to be released.

Bibliography

1. Theis, E. R., Nayudamma, Y., and Kritzinger, C. C., *J. Amer. Leather Chem. Assoc.* **46,** 220, (1951).
2. Gustavson, K. H., *ibid.*, **22,** 60, (1927), *ibid.*, **19,** 446, (1924).
3. Merrill, H. B., Niedercorn, J. G., and Quarch, R., *ibid*, **23,** 187, (1928).
4. Thomas, A. W., *ibid.*, **15,** 504, (1920).
5. McLaughlin, G. D., and Theis, E. R., The Chemistry of Leather Manufacture – A.C.S. Monograph, Reinhold Publishing Company, 1945.
6. Theis, E. R., and Meerbott, W. K., *J. Amer. Leather Chem. Assoc.*, **36,** 293, (1942).
7. Thorstensen, T. C., and Theis, E. R., *ibid.*, **47,** 588, (1952).
8. Fiegl and Kraus, *Ber.* **58B**, 398, (1925).
9. Blaedel, W. S. and Panos, J. J., *Anal. Chem.* **22,** (910) (1950).
10. Theis, E. R., and Thorstensen, T. C., *J. Int. Soc. Leather Trades Chem.* **31,** 124, (1947).
11. Serfass, E. J., Theis, E. R., and Clark, A., *J. Amer. Leather Chem. Assoc.*, **42,** 369, (1947).
12. Ueberbacher, E. and Droscher, K. *Collegium* **832,** 433, (1939).

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BOOK NOTICE

Planning and Making Industrial Waste Surveys. A publication of the Ohio River Valley Water Sanitation Commission, 1952. (Price $1.00). This manual was prepared by the Metal-Finishing Industry Action Committee. The Introduction states "This manual is not a treatise on the theory of flow measurement. It is a 'how-to-do-it' description prepared for the use of operating men whose normal duties may be quite remote from the conduct of

a waste survey but who, nevertheless, may be called upon to do the actual job." It is divided into five parts: Planning the Waste Survey. This part generalizes on the importance of determining the concentration volumes, sewer maps, means of tracing flows, and the duration necessary for an accurate survey. How to Measure Flow. A detailed description of the various methods used in measuring volumes, such as bucket and stop-watch, open-end pipe flows, California-pipe flow method, depth and velocity of flow in partly filled sewers, salt concentration, various types of weirs, and the Parshall flume. How to Take Samples. The importance of proper sampling is emphasized and details given for sampling and compositing. How to Calculate Waste Load. This includes the formulas necessary and gives examples to simplify the calculations. Appendix. Seven tabulations for calculating volumes by the different methods described are given. This is a very useful and practical manual.

J. F. W.

ABSTRACTS

Studies of Sedimentation Basin Design. By T. R. Camp. *Sew. and Ind. Wastes*, **25**, 1 (1953). A cardinal principle in the functional design of sedimentation basins is to provide sufficient floor area to receive the particles to be settled out. This principle was first announced to the sanitary engineering profession by Hazen in 1904. The author has explained this principle again in simple terms and discusses other principles which determine the shape of sedimentation basins for best performance of their function. Eight references.

J. F. W.

Facts and Fallacies of Sedimentation. By L. B. Escritt. *Surveyor*, **111**, 203 (1952). Through *Sew. and Ind. Wastes*, **25**, 120 (1953. Although sedimentation has been long used, and much studied, as a means for the removal of suspended solids from both sewage and trade wastes, the interchange of knowledge on the subject has not been satisfactory. The empirical rules of design, which were used very generally until recently, and which still have considerable influence, lead to results which are usually sufficient, but to poor economy of construction. If it is necessary to increase the detention period to remove a particle, it must be done by increasing the surface area, since an increase of depth, although it increases the detention period, proportionately increases the distance through which the particle must fall. Experiments have shown, however, that the efficiency of sedimentation varies as the fourth or fifth root of the surface area of the tank. Great changes of surface area, therefore, produce relatively small changes of efficiency. There are other means by which the efficiency may be increased more economically. The inlet must be of such type that the velocity head of the sewage is dissipated, as much as possible, before the sewage enters the tank, and the sewage must enter at low velocity. Both the inlet and the over-all proportions of the tank must be designed to avoid velocities high enough to cause turbulence of such intensity as to interfere with sedimentation. The position of the outlet weir may greatly affect the efficiency. The best arrangement is to remove the effluent in a thin film from the surface, in a position where the least concentration of suspended solids exists. The usual arrangement of having the outlet weirs at the top of the tank walls is not ideal, since currents impimping on the walls below the weirs cause comparatively high upward velocities, tending to lift sludge toward the weirs. A better arrangement is to have the weirs at a distance from the walls, so that sludge lifted by the currents at the walls may settle again before reaching the weirs. Particles too small to settle may flocculate, or gather together into clumps of settleable size. This action can be encouraged by the use of chemical coagulants or by gentle stirring. The upward flow tank takes advantage of this effect by pass-

ing the entire mass of liquid through a sludge blanket, which in effect strains out many particles too small to settle by themselves. The velocity of upward flow must be less than the falling velocity of the sludge. Upward velocities at maximum flow of from 4.5 to 9 feet per hour are the values commonly used in design.

The Drying of Hides and Skins. By J. R. Furlong. *Colonial Plant and Animal Products*, **2**, 233 (1951). The present article reviews the progress that has been made over the past twenty years in experimental and practical drying of African hides and skins. It was found that the essential condition for the correct drying of hides and skins was the free circulation of air on both sides of the hide or skin. It is known as suspension drying. It was also found that the sun was in no way detrimental to the stock being dried, and shade was not essential to the production of good quality. No material difference was found in hides or skins preserved by dry salting, shade drying and sun drying by suspension. When stock was thrown over a pole, destruction often occurred where the pole and stock contacted. It is believed that ground drying leads to putrefactive decomposition and gelatinization of the hide fibers. Degradation terminates with the completion of the drying operation. Slow shade drying during the rainy season can also lead to putrefactive decomposition of the stock, therefore speed in drying seems to be an essential characteristic in the manner of pelt preservation. Over drying leads to fiber structural change. Goat skins dried on frames or over lines were found to be equally satisfactory. It is believed that there may be a maximum temperature for the successful drying of sheep and goat skins and evidence was obtained to conclude that a shade temperature of 109°F. was too severe for sheep skins but this will be confirmed by additional tests.

Sheep skins are removed from the carcass in cased form; hence a different procedure must be followed in their drying. The skins, turned inside out, are suspended between sticks at a distance of 6-8 inches from the ground, in the open. In this manner, one side is fully exposed to the sun, while the other is toward the ground, and consequently in the shade. No ill effects due to exposure to the sun have been observed. It is to be noted, however, that the skins are usually taken down in the afternoon before they are fully dry and transferred to a lock-up room. The last stages of drying take place in the dealer's store where the skins are hung in bunches.

Utilization of Sharks. By D. E. Reader. *Colonial Plant and Animal Products*, **2**, 275 (1951). Shark meat, oil, fins and skins all find commercial use. The greatest user of the skins is the United States. Imports from 1945 to 1950 varied from 48,000 pounds to 187,000 pounds. The Carribian area supplied the greatest quantity. The most valuable shark for its skin is the Nurse Shark, but good quality skins from other species are obtainable at slightly lower cost. Skins less than 4 - 5 feet in length and those with bad fighting scars on the belly are valueless. Fleshing is more readily carried out after the skins have been brined for 3-4 hours. They are then washed in sea water, salted down in piles 3 - 4 high and cured for 4 - 6 days. They are then shaken free from loose salt, new salt applied, folded flesh side in, made into flat bundles and packed in sisal bags, barrels or packing cases, according to market requirements. Damage to the skins can come from contact with fresh water during the brining and curing stages. Such damage is known as sour spots. Other causes of sour spots are delay in skinning after death, lack of quick and thorough curing, and poor quality salt. Sour spots are really decayed spots. Burnt skins are those which have deep wrinkles not removable by the tanning process. These wrinkles are caused by not laying the skins flat during the curing or by exposure to hot sun. Even overheating during storage may produce this defect.

The Use of Acacia Pods and Bark as Tanning Materials. By W. D. Raymond, *Colonial Plant and Animal Products*, **2**, 285 (1951). Acacia pods form an important material in African countries, while the bark constitutes the principal tanstuff of Northern India, but so far they have not found much application outside the countries named. They are derived from *Acacia arabica*, a moderate sized, almost evergreen tree, indigenous to large areas of Asia and Africa. While the tree is regarded as of medium size, it may vary from little more than a shrub in some areas to a tree of 8-10 feet girth in other districts. The pods are 3-6 inches long, 0.5 inch wide and carry 8-12 seeds. The pods were used even in Pliny's time for tanning. The bark and pods are known by a variety of names and appear on the market from time to time under one or another. Some of the main variants are: Babla (Arabic), Babul (Hindustan), Babar (Sind), Sant or Sunt grains or Garad pods (Sudan), Gonaike or Neb-Neb (French West Africa), Gabaruwa or Bagaruwa (Nigeria). Sudanese pods can be dissected into percents as follows: seeds 33, inner pod coat 12, outer coat pod 23, resin-like grains between the pod coats 32. The grains have the highest tannin content, and the seeds the least. The latter, however, contain troublesome sugar which ferments and causes rapid deterioration of the tan liquor. Indian pods from which the seeds have been removed contain 18-27 percent tannin, but the Sudanese material contains 30 per cent or more. Cause for this variation is related to climate and soil. Ripe pods are considered richer in tannin than the green ones. Since the grains are richest in tannin, attempts have been made to concentrate these by mechanical means, but such attempts have not been successful. An objection by European tanners to sant grains or pods lies in the high proportion of mineral matter present (4-5.4 per cent ash). Leather produced by sant pods is soft and light colored. Native produced leather in the Sudan and Nigeria has a high reputation for durability, especially in the bookbinding trade. Some of the best Nigerian tanned sheep skins are of sufficiently good quality to be suitable for the manufacture of gas meter leather. The tannin in the pods gives a blue to violet coloration with ferric salts and yields gallic and ellagic acids and phlobaphenes with acid. One of the fission products obtained is pyrocatechuic acid, so for the present it is probably best classed as a mixed tannin. Because of the high iron content of liquors made from saut pods, United Kingdom tanners do not care to use the material, fearing spotting of the leather.

Babul bark has constituted the most important tanning material in Northern India. It is usually employed in small village tanneries. It contains about 12 per cent tannin with a tan to nontan ratio of 1.5 to 1.0. Bark from trees 5-10 years old is preferred as old bark yields a darker color of tannin. An acre of ground will, in 15 years, yield as much babul bark as a like area of wattle in 7-9 years. The annual bark requirements for Northern India were 100,000 tons up to 1940, but since that time wattle extract has been supplanting the bark. Since 1950, however, there has been a decrease in wattle consumption, and a corresponding increase in babul bark usage. Babul bark tans slowly, producing a dark colored leather, but with suitable pH control of the process, the leather is suitable for sole and heavy duty purposes.

Drying Trials with Goat Skins in the Sudan. By J. R. Furlong. *Colonial Plant and Animal Products*, **2**, 205 (1951). Skins were received in case form from local slaughterings, prepared and dried as follows: (1) washed, opened down the belly and shanks, stretched on frames by tacking, dried in the shade under a shed with good air conditioning; (2) skins prepared as in the first case, then hung over thin rope to dry, flesh side out, in the shade under a shed; (3) skins prepared as in first case, then stretched on frames and dried in the full sun; (4) skins prepared as in the first case, then hung over thin rope, flesh side out, in full sun to dry. The minimum and maximum temperatures during the drying period were 49°F. and 97°F. respectively, and lowest and highest relative humidities were 7 and 50

per cent respectively. All drying methods gave satisfactory results as demonstrated by the leather produced from the skins. Because of its simplicity, drying over thin rope in the sun is recommended, especially during the cool season. In hot weather some form of shade should perhaps be provided.

Alphabetical List of New Products Developed Since November, 1951. Dyestuffs and Pigments, Textile Chemicals, Equipment. *Amer. Dyestuffs Reporter*, **41**, 795 (1952). As the title indicates, a listing has been made of new products and equipment. A short description is given of each product, and the name of the manufacturer.

Data Pertaining to the Change of Shrinkage Temperatures in the Vegetable Sole Tanning Process. By G. Vago and I. Feher. *Shoe and Leather Industry*, **1**, 104 (1951). Through *Hungarian Technical Abstracts*, **4**, 93 (1952). When using tanning liquors made from synthetic tanning material and valex, a temporary fall at the point of shrinkage of the leathers was discernible. This can be attributed to the weakening of the firmness of the bonds holding the collagen main chains together caused by the adsorption of surface active materials. The point of shrinkage rises somewhat later when the surface active material succeeds in establishing a linkage on several polypeptide main chains; new bridge-linkages are formed which lead to tanned collagen, having a more stable space lattice. A number of experiments with valex juice and tannin resulted, during the first few days of the tanning, in reducing the point of shrinkage by 2 to 6 degrees. The practical conclusion to be drawn from these experiments is that if thick crops are placed into the hot pit without being completely processed, the resistance to bursting of the middle layer of the leather shows a sudden drop.

Fur Dyeing. By F. Brugger. *Leather and Shoe Ind.*, **1**, 38 (1952). Through *Hungarian Tech. Abst.*, **4**, 94 (1952). Fur dyeing can, in general, be divided into three very complex operations. The pre-treatment consists of degreasing and swelling the hairs by the use of lyes and oxidizing agents. In other instances, the fur is bleached by reducing or, more often, by oxidizing processes performed in baths or by a brush. Pickling in a solution of various metallic salts precedes the dyeing. This can be done with extracts of vegetable origin, prepared chiefly from woods, applied through baths or by brushing. From the inorganic materials, only lead salts are used for dyeing in the form of sulphides precipitated directly upon the fibre. The synthetic dyestuffs are most widely used, and among them primarily the oxidizing dyes. The latter are formed on the fur proper through the oxidation of aniline and other amines with chromic acid or hydrogen peroxide. This form of dyeing results in the most diverse effects reminiscent of high-grade furs.

Resistance of Sole Leather to Wear Examined by Solyom-Barna Wear Testing Machine. By A. Laszlo. *Shoe and Lea. Ind.*, **1**, 35 (1951). Through *Hungarian Tech. Abst.*, **4**, 94 (1952). The Solyom-Barna wear-testing machine does away with the well-known shortcomings of other similar apparatuses, namely that the wearing surface, especially when emery paper is used, is not constant, and a picture cannot be obtained either of the entire worn-off volume or of the individual layers of the leather. The essence of the machine consists in that it is possible to set the volume to be worn off beforehand according to what is desired, and this having been set constant, the time required for the wear is determined. On the basis of approximately 300 tests conducted by the Leather Research Institute, it has been established that sole leather can be well worn off in 0.2 mm. layers.

Before subjecting the leathers to the tests, they must be soaked in water for 24 hours (to extract all the chemicals therein) and completely dried. The right and left sides of the leather treated by different methods as well as fibre leathers and artificial leathers give good comparative values. It must be noted that the Solyom-Barna wear-testing machine was originally designed for the rubber industry.

Influence of Slow or Rapid Tanning Methods on the Chemical Constitution, Physical Properties and Stability on Aging of Vegetable Tanned Sole Leather. By F. Stather and H. Herfeld. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.* No. 2, 31 (1949). Data previously reported [see *This Journal*. **47**, 681 (1952)] on properties of commercial sole leathers, produced by different tanning procedures, is of questionable validity because of lack of information about the kind of raw stock employed. The present test was carried out with 144 cattle hides, of which 72 were North German (30-35 kg.) and 72 were South German (35-40 kg.). Half the skins from each district were cow hides and half were ox hides. All were cropped to yield a total of 288 bends. They were divided into 9 lots of 32 bends, each containing 16 lefts and 16 rights, 16 cow hides and 16 oxen, and 16 North and 16 South German bends. Each bend was marked for future identification. Each lot was tanned in a different tannery, by commercial methods that differed widely. The processes are classified into 2 groups as follows: *I*, slow tannage (7-12 months) with weak liquors exclusively (1.8° to 4.4° Be′ max.), 4 tanneries; *II*, slow or rapid tannage (1½ to 10 months with strong liquors, 7° to 16° Be′) at some stage of the process (5 tanneries). Nothing is said about beamhouse treatments, which apparently differed between tanneries, because average white weight, as % of soaked weight, varied from 81 to 92. Average finished weights, for all tanneries, as % of soaked weight, were slightly higher for ox hides (58.7) than for cow hides (57.6), and considerably higher for South German (60.4) than for North German hides (55.6). There was no clear cut difference in weight yields between tannages *I* and *II*. In general, finished weight, as % of soaked weight, increased with time of tannage and with maximum tannin concentration, for both types of tannage. Thus, the highest weight yield (65%) was obtained by tanning for 1½ months, partly in the drum, with liquors up to 11° Be′, the next highest (61%) by tanning for 10-12 months in liquors up to 1.8° Be′, the lowest (51%) by tanning 7 months in liquors up to 4.4° Be′. Results of chemical analysis showed that degree of tannage, and % ash were generally, and % water solubles was always, higher for *II* than *I*; pH value of water extract generally was higher for *I*. Degree of tannage was considerably higher for the North German skins than for the denser South German skins, but no difference in degree of tannage was found between ox hides and cow hides. Analysis of grain, middle and flesh splits showed no definite difference between *I* and *II* with respect to the differences in fixed tannin, total water solubles, free water solubles and combined water solubles between middle and surface splits. Two series of wear tests on a walking track led to quite variable results, but on the average the soles from the two longest tannages (12 and 11 months) gave the best wear, and the soles from a very rapid tannage (1-5 months) gave decidedly the poorest wear. However, the average life of soles from a 7 months' tannage was as great, and that for soles from 2-5 months' tannage was almost as great as the average life of the soles from 11 and 12 months' tannages; conversely the soles from a 10 months' tannage had an average life very little longer than those from the shortest tannage (1-5 months). Taken as a group, the leathers from tannage *II*, having an average degree of tannage of 75, and tannin: organic water solubles = 2.6, wore through about 10% sooner than the leathers from Tannage *I* (average degree of tannage = 63, tannin: organic water solubles = 5.1). These results were confirmed by the Stather-Herfeld wear coefficient, though the latter indicated a much greater difference than did the practical wear test. No damages took place in any of the leathers

on normal storage for 2 years, other than a small increase in combined tannin at the expense of water solubles. Tensile strength actually increased slightly. The accelerated aging test, in moist O_2 at 35°C., for 6 months, resulted in an average loss in tensile strength of 15% for leathers of Tannage *I* and 19% for leathers of Tannage *II*. The validity of this accelerated aging test is questioned, since the results do not agree with those found on prolonged normal aging. On exposure to the weather for 1 year, the leathers of Tannage *I* lost 13%, and those of Tannage *II*, 18% of their average initial tensile strengths. For both types there was the expected loss of water solubles due to leaching by rain, but, curiously, degree of vegetable tannage increased at first, later declining to about the original values. H. B. M.

Comparative Evaluation of Statistical Analytical Data for Vegetable Tanned Sole Leathers of Slow Pit Tannage and Accelerated Pit-Drum Tannage. By F. Stather and H. Herfeld. *Ges. Abhandl. deut. Lederinsts Freiberg/Sa.* No. 4, 39 (1950). Analytical data for 791 commercial sole leathers are tabulated. The leathers are classified, according to type of tannage, into 3 groups: (*I*) pit tannage for 10 to 12 months, (*II*) pit tannage for 7 to 9 months, and (*III*) moderately accelerated combination pit and drum tannage for 4 to 6 months. All 3 types varied widely in composition and there were no sharp differences in composition between the types. However 89% of the leathers of Tannage *I* and 65% of Tannage *II* contained less than 9% water solubles, and 86% of the leathers of Tannage *III* contained more than 9% water solubles. A value for "leathers substance" (hide substance plus fixed tannin) below 74% (14% water basis) almost certainly indicates a leather of Tannage *III*, but the converse does not hold true. No consistent difference between types of tannages were found for pH value, fat content or degree of tannage. Ash content tends to increase from Tannage *I* to Tannage *III*. No leathers of Tannage *I* contained over 1.5% ash, but many leathers of Tannage *II* and *III* had equally low ash contents. No definite difference between leathers of the different tannage types were found with respect to specific gravity, strength, stretch, water absorption, water transmission, air permeability, water vapor permeability, or wear resistance. H. B. M.

Slow or Rapid Tanning Procedures for the Production of Vegetable Tanned Bottom Leathers? By Fritz Stather. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.* No. 4, 45 (1950). This is discussion and review with 93 references. Most publications on the subject fail to provide any real comparison between slow and rapid tannage. The procedures used are variously described, the descriptive terms are inadequately defined and the numerous variable factors are inadequately controlled. In practice, the slow tannage (12 to 18 months) is most often applied to heavy, dense hides, and the rapid tannage to lighter hides. The slow tannage generally follows a dehairing process (sweating, or brief liming) that has very little opening-up action on the hide fibers, and skins destined for the slow tannage are seldom delimed and never bated. Further, the slow tannage is accomplished mostly with vegetable tanning materials of low purity. In contrast, skins to be tanned by the rapid processes are given a more prolonged liming, are generally delimed, frequently given a superficial bating, and are tanned mostly with high purity tanning extracts. The maximum strength of liquors used in the slow tannage never exceeds 5° Be′, compared to 15° Be′ for rapid tannage; and rapid tannage often involves drumming and use of elevated temperatures. The post-tanning operations are also different. The principal differences in the tannage proper are: concentration of tannin, acidity, temperature, and time of tannage. These factors influence fundamentally such properties of the liquor as dispersity, rate of diffusion into hide, rate of take-up, degree of combination and irreversability of combination. The effects of these differences in conditions of tannage, separately and in combination, on

the properties of the liquors, are discussed, without establishing any definite differences between slow and accelerated tannages, especially since the slow tannage generally is done with less astringent tanning materials. Findings of other workers as to differences in chemical constitution and physical properties between leathers from slow and accelerated tannage are reviewed. Much of this work is of limited value, either because of scanty data or because the actual tannage conditions were unknown or not stated. However, even the conclusions drawn by careful workers from extensive and sound data are not in agreement. From the scientific and technical standpoint, the question of slow versus accelerated tannage could be answered if we knew which chemical and physical properties are associated with best performance in use, and how these properties are affected by the tanning method, bearing in mind that some properties are obviously more important than others. Quality in general, declined with increasing mineral matter content, but this effect is not appreciable unless mineral matter exceeds 2.5%. While leathers made by accelerated tannage contain more mineral matter than those from slow tannage, they need not and should not contain more than 2.5% ash. Similarly, leathers from accelerated tannage contain more fat, but this is not objectionable unless the fat content exceeds 2%. The percentage of organic water soluble matter in sole leather depends in the first instance on the concentration of the final liquor; hence leathers from accelerated tannage generally, but not always, contain more water soluble matter than leathers from slow tannage, depending on how thoroughly they are washed. A high content of water solubles, results, temporarily, in enhanced stand, and reduced flexibility, water uptake, water transmission, air transmission, and wear resistance, but these properties are lost rapidly during use under wet conditions. The water soluble matter content of leather from accelerated tannage should not exceed 16% (butt), 18% (neck), and 20% (belly). Leather from slow tannage with weak liquors always contains water soluble matter below these limits, but it is not true that such leather is invariably better in quality than leather from an accelerated tannage, containing slightly more water soluble matter. The fixed tannin content bears no relation to the duration of tannage, since the effect of shorter time is off-set by higher tannin concentration and temperature. Leather from slow tannage frequently, but not necessarily, contains more hide substance but a clear cut relationship between hide substance content and physical properties or value in use has not been established. Degree of tannage generally is higher (70-95) for leathers of accelerated tannage (provided the time of tannage is not too much curtailed) than for leathers of slow tannage (frequently 60-70). Both very low (under 60) and very high (over 95) degree of tannage are undesirable. Analytical figures can be used to determine the method of tanning as follows:

	Slow tannage	Accelerated tannage
Leather substance (hide substance + fixed tannin)	Over 75	Under 75
Organic water solubles per 100 leather substance	Under 10	Up to 18
Combined tannin: organic water solubles	Over 3	Under 3

But these figures tell nothing about the relative merits of the two leather types. Attempts to establish a connection between type of tannage and physical properties of sole leather have led to largely negative results. Micro-structural differences between slow and rapid-tanned leathers are detectable only when rapid tannage is accomplished by excessive drumming. It is possible to make just as good sole leather by accelerated tanning methods as by the very slow methods, providing the reduction in time and increase in liquor concentration are not too extreme. The nature of the hide, and the pre-tanning and post-tanning operations, have much more influence than the tanning method on sole leather quality. Economically, the slow process possesses nothing but disadvantages (capital tie-up, poor tannin utilization, loss of tannin by oxidation or fermentation). The primary reason why leather of slow tannage still enjoys a higher reputation is that this process is almost certain to produce a high quality sole leather, while considerable leather of low quality is, or was, produced by accelerated tannages, when the proper conditions have not been worked out. H. B. M.

Slow or Rapid Tannage in the Production of Vegetable Tanned Bottom Leather? (Critical discussion of a polemical address and progress report by A. Küntzel). By F. Stather. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.* No. 8, 45 (1952). A reply to Küntzel [*Das Leder*. **2**, 32, 54, 83 (1951)], who disagreed with Stather's conclusions (see preceding abstract). K. appears to assume the superiority of leather made by the slow tanning process. S. does not question the merits of such leather, but believes that equally good leather can be made by the modern, accelerated process, provided that the time of tanning is not shortened too much. K. differs from S. in conception of what constitutes the fundamental difference between the old, pit process and modern tanning. S. defines the former as a tannage carried out exclusively with weak, fermented liquors, tending to give acid swelling, prepared by cold extraction, without mechanical action or use of elevated temperature, and consequently requiring a long time for completion. K. regards most of these characteristics as unimportant, and holds that the essential characteristic of the old, slow process is the acid plumping before or during the initial stages of tanning. To K's suggestion that methods of evaluation are not sensitive enough to detect the difference between leathers produced by the old, pit tannage and by modern tannage, S. replies that the methods employed did show the inferiority of leather produced by *extremely* accelerated tannage, and consequently would have detected any significant differences between leathers produced by very prolonged and moderately accelerated tannages, if such differences really existed. H. B. M.

Influence of Temperature During Tanning with Vegetable and Synthetic Tannins. By F. Stather and H. Herfeld. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.* No. 3, 3 (1950). This is a study of the effect of temperature, in the range from 2 to 40°C., on the analytical characteristics of tan liquors, rate of tanning, and analytical characteristics of leather produced in small scale laboratory tests. The materials studied were: extracts of raw quebracho, spruce bark, wattle bark, oak wood, and chestnut wood; 4 synthetic replacement tannins: Tanigen Extra A, Gerbstoff QE, Gerbstoff KN, and Irgatan B; and Saxonia, (a commercial lignosulfonate). Tests were made at 1, 2, 10, 20, 30 and 40°C. Analyses made by the filter method showed that insoluble matter decreased markedly with increase in temperature for quebracho and chestnut, and for oak wood up to 20°, but was practically unaffected by temperature for spruce and wattle. The syntans and lignosulfonate contained no insoluble matter at any temperature. On the other hand, non-tannin increased with temperature for all the vegetable extracts, Tanigan Extra A, and Gerbstoff QE; decreased from 2 to 20° and increased from 20 to 40° for Gerbstoff KN and Irgatan B, and decreased with temperature for the lignosulfonate up to 30°, increasing again at 40°. The net effect on tannin con-

tent is a considerable increase with temperature for quebracho and lignosulfonate, a decrease with temperature for spruce, wattle, oak wood, Tanigan Extra A and Gerbstoff QE, practically no change with temperature for chestnut, and maximum tannin content at 20° for Gerbstoff KN and Irgatan B. The increase in non-tannin content with temperature is ascribed to decreased average size of the molecular aggregates. Further tests were made with stronger liquors (1, 2.5, 5, 7.5 and 10° Baume'), in which the volume of sludge was measured after 72 hours' settling. Of the four syntans and lignosulfonate only Gerbstoff QE produced measurable sludge at any concentration, although Tanigan Extra A gave turbid solutions. The volume % of sludge, at 20°C., increased with liquor concentration for quebracho and oak extracts (but not linearly); for wattle and chestnut the volume % of sludge was practically constant for 5° Baume' liquors and stronger; for spruce extract, volume % sludge was maximum in 2.5° Baume' liquors and declined to zero in 10° liquors. The effect of cooling to 2° and heating to 40°, on increasing or decreasing the volume % of sludge, was greater for the more concentrated liquors (quebracho, oak, chestnut), but was most marked for 2.5-5° liquors in the cases of spruce and wattle. Salting out values [*This Journal*, **47**, 630-1 (1952)] i.e., fraction of total tannin precipitated by salt at 1/3, 2/3 and complete saturation, diminished with increasing temperature for all the materials. The effect of cooling from 20° to 2° was generally, but not always greater than the effect of heating from 20° to 40°. Tan value [*This Journal*, **47**, 629-30 (1952)] decreased with increasing temperature of tanning, for quebracho, wattle, oak and chestnut, when the solutions were clarified at 20°, because of precipitation of insoluble matter at the lower temperatures; when the solutions were clarified at the temperature used for tanning, tan value increased with temperature for all the extracts. This increase was large for quebracho and spruce, and for chestnut up to 20°, and small for the other extracts. Combining value (loc. cit.) increased with tanning temperature for all extracts. The effect was most marked above 20°, and was greatest for quebracho, moderate for oak and chestnut, and smaller for the others, especially the syntans. Rate of penetration into skin, rate of tannin fixation, degree of tannage after 16 weeks, and irreversibility of tannage [*This Journal*, **47**, 664 (1950)] all increased with temperature. In general, the affinity of collagen for tannin, as well as the degree of dispersity of the tannin, increases with temperature. These temperature effects generally are smaller for replacement syntans than for natural tannins. H. B. M.

The Influence of Tanning Method and Intensity of Tannage on the Properties of Vegetable Tanned Leathers. By F. Stather and R. Schubert. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.*, No. 3, 31, (1950). The object of this work was to determine the effects of time of tannage, concentration of tannin, ratio of tannin given to pelt weight, and pH value of the tan liquors on leather yield, rate of tanning, degree of tannage, vertical distribution of tannin, and physical properties of the leathers. This work was done because previous comparisons, of commercial leathers tanned by slow and rapid tanning procedures [see *This Journal*, **48**, (1953)] are of questionable validity because of unknown differences in the commercial processes employed. Six North Bohemian cattle hides were unhaired with $Ca(OH)_2$ and Na_2S, washed, cropped, split to 5 mm., and delimed completely with $(NH_4)_2SO_4$. The entire double bend areas, except the backbone strips, were cut into pieces (25 x 30 cm.), and 2 pieces were taken for each of 19 tanning tests. The tanning material used was a blend of equal parts, on tannin basis, of spruce bark, oak wood, and chestnut wood extracts. Analytical characteristics of this mixture agreed with values calculated from those of the components, except that actual combining value, and actual fraction precipitated at 1/3 saturation with salt, were somewhat higher than calculated. In all tests, the pieces were tanned initially in 200% liquor containing 0.5% tannin (0.5 day), 1.0% (0.5 day),

1.5% (1 day), 2% (1 day), 2.5% (2 days), and 3.0% (3 days). Thereafter the pieces were handled as follows:

Series	I	II	III	IV
Concentration of liquor, %	6	3, 6, 9, 12	6	6
% tannin given on white weight	50	50	50, 37.5, 25, 12.5	50
Time in liquor (mo.)	1, 2, 3, 4, 5, 6, 8, 10	3	3	3
pH value of liquor	4.1	4.1	4.1	3.1, 4.1, 5.1

In series II, the pieces to be tanned in 9 and 12% liquors were passed through liquors containing 6%, and 6 and 9% tannin respectively, before entering the final liquor. The concentration of the final liquors were maintained constant by periodic analysis and strengthening (therefore, the actual percentages of tannin given on white weight were considerably higher than indicated above). Mold growth was inhibited by Preventol. All tanning was done by suspension in still liquors, at room temperature. After tanning, the pieces were drained, rinsed 1 hr. in 600% water, slicked by hand, lightly oiled, dried at 20°C., and rolled. A tannin balance sheet is given, taking into account the tannin lost as insoluble matter and in the rinse water. Tannin not accounted for was less than 5% of the amount given, except in 1 experiment. Yield values (finished weight, 14% water, as % of the white weight) increased in Series I from 69 for 1 month to 76 for 6 months, and showed no further increase at 8 and 10 months. In Series II, yield value increased from 67 for 3% tannin concentration to 72 for 6% and 75 for 12% concentration. In Series III, yield value declined from 75 for 50% given tannin (actually 85%), to 61 for 12.5% given tannin (actually 29%). In Series IV, yield values for pH values 3.1, 4.1 and 5.1 were 76, 72 and 71 respectively. It is noteworthy that corresponding members of Series I, II and III, tanned under identical conditions, gave yield values varying from 68.4 to 75.0. Degree of tannage increased in Series I from 58 (1 mo.) to 94 (10 mo.); in Series II from 74 (3% liquors) to 87 (12%); declined in Series III from 76 (50% tannin) to 47 (12.5%); in Series IV from 91 (pH3.1) to 72 (pH = 5.1). Percentage of organic water solubles (on hide substance basis) showed no definite trend with increased time of tanning (Series I), but increased with liquor concentration (Series II), with amount of tanin given (Series III), and with increasing pH value (Series IV). Ratio of fixed tannin to organic water solubles increased with time of tanning (Series I), decreased in Series II from 6.3 for 3% liquor to 3.3 for the 6, 9 and 12% liquors, increased slightly with amount of tannin given (Series III), and in Series IV was 5.2 for pH 3.1 compared to 3.3 and 3.6 for pH values of 4.1 and 5.1 respectively. Ratio of degree of tannage of grain splits to degree of tannage of center splits was independent of time of tannage, concentration of liquors, and pH, but was considerably higher for the leathers given only 12.5 and 25% tannin (Series III). Ratio of organic water soluble matter in grain split to organic water soluble matter in center split was independent of time of tannage (after 2 mo.), increased with concentration of liquor and with amount of tannin given, and was unaffected by change in pH. Rate of penetration

of tannin into hide was independent of liquor concentration, but increased markedly with increase in pH value. Physical tests showed that water absorption, air porosity, water vapor transmittance all decreased, and thermal conductivity increased with increasing degree of tannage, but no definite relationship was found between degree of tannage and tensile strength, stretchability, stitch tear resistance, specific gravity and wear resistance.—H. B. M.

Influence of Wetting and Dispersing Agents on the Qualities of Vegetable Tannin Solutions and their Behavior during Tanning. By F. Stather and R. Schubert. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.*, No. 4, 69 (1950). The addition of wetting and dispersing agents to vegetable tan liquors is said to shorten the tanning time, give better utilization of tannin, and improve the leather quality. However, no data supporting these claims has hitherto been published. Eighteen surface-active agents were studied, including "Molvenin" (a protein decomposition product), sulfated castor oil (low, medium and high degree of sulfation), fat alcohol sulfonates of chain length varying from 4-6 to 16-18 C, "Pekoral L" (a sulfonate of fat acids and higher alcohols), "Merpin W" (an alkyl naphthalene sulfonate), "Emulgator TC" (a quarternary ammonium compound), "Lamepon A" (a fat acid-protein condensate), "Nekal BX" (a naphthalene sulfo-acid), phenol sulfonic acid, naphthol sulfonic acid, Neradol ND, and a commercial lignosulfonate. The tannins studied were non-sulfited quebracho, spruce bark, and oak wood extracts. Preliminary tests showed that best results were obtained when the tannin and the surface-active agent were dissolved together in hot water. The effect of surface-active agents on insoluble matter was studied by preparing solutions containing 1 to 10% tannin and 1 to 5% surface-active agent on the dry extract weight, adjusting pH value to that of the tannin alone, and determining insoluble matter as the difference in total solids before and after centrifuging. For quebracho (1% tannin) the presence of 1% surface-active agent reduced the insoluble matter by 25 to 60%. The result with 5% surface-active agent was seldom better, and sometimes worse, than with 1%. For quebracho (10% tannin), the surface active agents tended to increase the insoluble matter. Best results with quebracho were obtained with sulfated castor oil (medium degree of sulfation), fat alcohol sulfonate (16-18 C), Emulgator TC, and Lamepon A. None of the agents had a worthwhile effect on insoluble matter in spruce bark or oak wood extracts. Similar results were obtained by measuring the volume of sludge in non-centrifuged solutions. The surface-active agents (up to 10%) had practically no effect on the precipitation of quebracho and oak wood extracts by NaCl, and increased the fraction of spruce bark extract precipitated at 1/3 NaCl saturation. The effects of the surface-active agents on tan values and combining values were specific with respect to the particular tannin and the particular agent. All the surface-active agents (10% on dry extract weight) increased the tan value of quebracho, from 91 to 97-100, but only phenol sulfonic acid, naphthol sulfonic acid, Neradol ND and the lignosulfonate increased the tan value of spruce bark extract appreciably, from 66 to 70-73, and only the fat alcohol sulfonate (16-18 C), phenolsulfonic acid and naphthol sulfonic acid increased the tan value of oak wood extract, from 85 to 90-93. All the agents increased the combining value of quebracho, from 47 to 49-64. None of the agents increased the combining value of spruce bark extract appreciably, and some decreased it. For oak bark extract, the combining value was increased from 44 to 49-51 by fat alcohol sulfonate (16-18 C) naphthol sulfonic acid and Neradol D, while the other agents gave small increases or decreases. As an example of specificity, fat alcohol sulfonate (16-18 C) increased the combining value of quebracho from 47 to 53, decreased the combining value of spruce bark from 40 to 35, and increased the combining value of oak wood from 44 to 47. For strongly sulfated castor oil, the changes in combining value were: quebracho 47 to 64, spruce bark 40 to 38, oak wood 44 to 42. Effect of surface-acitve agents on rate of penetration was measured with strips of delimed cattle hide hung in 5% tannin solution containing 1 to 10% of agent (on dry extract weight), at the normal extract pH

value. Time is recorded in days for 50% and 100% penetration, in the presence of 0, 1 and 5% surface-active agent. Again the effects were specific. All the surface-active agents, except Pekorol L and phenolsulfonic acid with quebracho, and lignosulfonic acid and Molvenin with oak wood, decreased the time required for 50% penetration. Pekorol L, phenolsulfonic acid, naphtholsulfonic acid and Neradol ND increased the time for 100% penetration of quebracho from 21 to 28 days, while all the other agents reduced it from 21 to 8-16 days. All the agents (except Molvenin, which had no effect) reduced the time for complete penetration of spruce bark extract, from 28 to 8-21 days. Six agents had no effect on time for 100% penetration of oak wood, while the others reduced the time from 28 to 10-16 days. The most generally effective agents were the fat alcohol sulfonates, Emulgator TC, Lamepon A and Nekal BX. The degree of tannage of the quebracho-tanned leathers, removed from the liquor as soon as struck through, was decreased by every one of the surface-active agents, from 65 to 37-63, while the degree of tannage of spruce-tanned and oak wood tanned leathers was sometimes increased, sometimes decreased and sometimes unchanged. The effect of the use of surface-active agents in tanning on water uptake of the leathers, and rate of wetting, was extremely irregular. In general, surface-active agents have a dispersing action on the insoluble matter of tanning materials, giving solutions that contain more than the normal proportion of high molecular weight tannins. The tan value and combining value is generally increased, as is the rate of penetration, especially in the early stages of tanning, but this does not bring about a higher degree of tannage. All these effects are highly specific both for the tannin and the surface-active agent. H. B. M.

Quality Requirements of Leather for the Shoe Industry. By G. Rheinberger. *Das Leder*, **3**, 247 (1952). A lecture, discussing problems of the shoe manufacturer, such as rubbing off of the leather dye or pigment, blisters caused by some component of the lining or cement, spotting when various colored leathers are being worked on the same machines, and shrinking of the leather during the manufacturing process. Sole leather should be light in weight, flexible, wear resistant, should take up little water and the tannin should be fixed so it will not stain the uppers when wet. After the use of hard rubber and substitute soles during the war there was a postwar demand for leather, but this was soon followed by numerous complaints of poor leather quality. The rubber sole manufacturers improved the quality and appearance of their product to make it acceptable to the user. This shows how important a conference would have been between the leather and shoe industries on the requirements of the shoe manufacturer. I. D. C.

Studies on Some Iron-Containing Sardine Oils. By V. G. Czepelak. *Oesterreichische Leder-Zeitung*, **7**, 113 (1952). A brown sardine oil, containing free hydroxy fatty acids (oil No. 1) was treated with a large amount of petroleum ether to precipitate and remove the oxidized fatty acids. This purified oil was designated as oil No. 2. Chamois leathers were tanned using the two oils. That tanned with oil No. 1 was rather stiff, while that tanned with oil No. 2 was moderately soft. The iron oxide contents of the oils and leathers were as follows:

	Oil No. 1	Oil No. 2
Iron oxide (Fe_2O_3)	0.0459%	0.0086%
	Leather No. 1	Leather No. 2
Bound fat (leather basis)	14.7 %	11.2 %
Iron oxide " "	0.024 %	0.0077%
Iron oxide (bound fat basis)	0.16 %	0.07 %

Since leather No. 1 contained 3.5 per cent more bound fat it is evident that free hydroxy-fatty acids, or iron soaps or both together increase bound fat and lower quality. Although oil No. 2 contained only a very small amount of iron the leather tanned with it was quite sticky. Small amounts of iron in highly oxidizable oils seem to be sufficient to cause stickiness. The active iron compounds are those dissolved in the oil and bound to oxidizable fatty acids and to hydroxy fatty acids. Compounds of iron and completely oxidized fatty acids are inactive. It may be possible to use dark oil containing iron for chamoising if it is mixed with a bright oil, the temperature is carefully controlled, and penetration of the skin is rapid and complete. I. D. C.

The Utilization of Spent Chrome Liquors. Anon. *Oesterreichische Leder-Zeitung*, **7**, 181 (1952). USSR technical report, abstracted from *Leder-Journal* No. 14 (1952) Bad Wörishofen. Spent chrome liquor can be used for pickling after adding salt and acid to bring it to the required concentration. The preliminary coloring with chrome salt in an acid medium brings about a uniform distribution of chromium. With the salt and bichromate that is saved the factory can pickle for six months and tan chrome leather for one month per year. I. D. C.

PATENTS

Process of Drying Gelatin Layers. U. S. Pat. 2,588,811. C. J. Dippel, J. A. Lely and J. O. M. Dikhoff, Eindhoven, Netherlands, assignors to Hartford Nat. Bnk. and Trust Co., Hartford, Conn. Appl. May 2, 1947. A process of drying gelatine layers, having a thickness when dried of less than approximately 100 microns comprising the steps of subjecting the gelatine layer containing water to an alternating electric field of high frequency having an intensity at which the gelatine is heated to a temperature at which it melts and the water removed therefrom within five minutes, and passing a gas stream over the gelatine layer to remove the water vapor expelled from the wet gelatine layer.

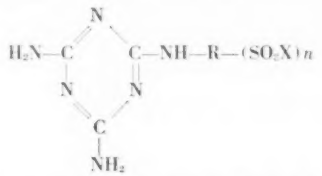
Resin Made from Tannin, Sulfuric Acid, Acetone, and Potassium Cyanide. U. S. Pat. 2,590,760. V. DaVeiga, SaoPaulo, Brazil. Appl. Apr. 27, 1948. The steps of heating in a closed vessel with 78 parts by weight of acetone and 42 parts by weight of cyanide of potassium the product of digesting 2 parts of tannin by weight in 150 parts by weight of concentrated sulphuric acid, and then adding sufficient tannin to restore the tannin to the amount originally present.

Method of Producing Gelatin Derivative. U. S. Pat. 2,591,133. D. H. Campbell, Altadena, J. B. Koepfli, San Marino and Linus Pauling, Sierra Madre Villa, Calif., assignors to California Institute Research Foundation, Pasadena, Calif. Appl. May 29, 1950. A method of manufacturing a gelatin product, which comprises condensing a gelatin solution in water by the addition of a condensation agent selected from the group consisting of carbon suboxide, formaldehyde, acetaldehyde, quinone and glyoxal, terminating the condensation before an irreversible gel has formed, oxidizing the condensed gelatin by the addition of hydrogen peroxide, adding salt to a concentration of approximately 0.9% and adjusting the pH to approximately 7.

Method of Treating Proteins with Saturated Aliphatic Polyamines and Resulting Product. U. S. Pat. 2,597,228. E. D. Cornwell, Downers Grove, and S. Dobija, Chicago, Ill., assignors to Armour and Company, Chicago, Ill. Appl. Jan. 6, 1949. A process for producing a water-soluble composition which upon drying will form a water-insoluble film, which consists of reacting a protein material selected from the group consisting of blood protein and egg protein in an aqueous solution with a saturated aliphatic polyamine at a temperature between 150 and 200°F.

Manufacture of Syntans. U. S. Pat. 2,597,809. J. Miglarese, Cincinnati, Ohio, assignor to The United States Leather Company, New York, N. Y. Appl. Sept. 8, 1948. The process of preparing a water-soluble tanning material which comprises dissolving water-insoluble soda lignin in a phenol in proportions from about 1 part of soda lignin to 2 parts of phenol to about 5 parts of soda lignin to 1 part of phenol, sulfonating the same by the gradual and progressive addition of concentrated sulfuric acid with stirring at a temperature around 50 to 60°C with subsequent increase in temperature to around 95°C to form a water soluble product, and reducing the acidity of the solution to a pH of around 3.5.

Tanning and Bleaching Leather with a Sulfoaromaticmelamine-Formaldehyde Resin. U. S. Pat. 2,599,142. J. T. Thurston, Riverside, and Pierrepont Adams, Glenbrook, Conn., assignors to American Cyanamid Company, New York, N. Y. Appl. Aug. 12, 1949. A process of tanning and bleaching which comprises treating hides and skins with an aqueous solution of a water-soluble acid-sensitive condensation product of 1 mol of a sulfonated aromatic hydrocarbon substituted melamine having the formula



wherein R is an aromatic hydrocarbon radical, X is selected from the group consisting of hydrogen, alkali metal and ammonium, and n is an integer from 1 to 3 with about 1 to about 5 mols of formaldehyde.

Shoe Insole. U. S. Pat. 2,599,317. David R. Brady, Detroit, Mich., assignor to Owens-Corning Fiberglas Corp. Appl. Aug. 2, 1946. A shoe comprising an upper, an insole made up of a plurality of layers of fibrous glass interwoven fabric impregnated with a thermosetting resin extending as a continuous body throughout the insole, and a layer of intermatted fibrous glass overlying the upper face of the insole and having a covering thereover, said intermatted fibrous glass having a resiliency providing a cushion for the foot of the wearer.

Apparatus for the Treatment of Hides, Skins, and the Like. U. S. Pat. 2,599,503. E. G. Wilson, Blundellsands, Liverpool, England. Appl. Apr. 11, 1951. Apparatus for the tanning of leather comprising in combination, a plurality of rollers journalled in a supporting frame and disposed one above another in two opposed series at opposite sides of a tan-

ning liquor containing pit, an endless horizontal conveyor band carried by and in respect of each opposed pair of said rollers, sprockets fitted at each end of certain rollers, a pair of endless chains arranged to move over and mesh with said sprockets whereby said chains follow a zig-zag travel path from top to bottom of the pit and from thence vertically upwards from bottom to top of the pit, lugs and attachment pins on certain link plates of said endless chains, battens having slotted end components for engaging with the attachment pins of said chains and to which battens pieces of leather to be tanned are secured, and means for actuating said apparatus automatically at controlled and gradually decreasing speeds.

Cements for Attaching Shoe Soles. U. S. Pat. 2,599,581. J. L. Perkins, Arlington, and E. E. Sylvester, Brookline, Mass., assignors to B. B. Chemical Co., Boston, Mass. Appl. April 2, 1948. A heat activatable cement comprising 100 parts by weight of a butadiene-acrylonitrile copolymer rubber containing from 25% to 45% of acrylonitrile, from 10 to 30 parts by weight of basic zinc carbonate, from 10 to 50 parts by weight of a resinous chlorinated paraffin hydrocarbon having a chlorine content of from 42% to 72% and having a molecular weight between 500 and 1060, and from 70 to 125 parts by weight of a copolymer of vinyl chloride and vinyl acetate containing from 85% to 90.5% of vinyl chloride.

Shoe Sole Composition. U. S. Pat. 2,600,461. Cecil F. Backus, Wilmington, Del. Appl. Mar. 17, 1949. A coating composition for spreading with a spatula or the like and having good adhesive and drying properties, and flexibility together with high resistance to cold-flow and wear in the dry condition, comprising 100 parts milled polychloro-2-butadiene 1.3 substantially insoluble in hydrocarbon solvent prior to milling and alone having optimum stickiness and a plasticity within the approximate ASTM number range of 280 to 355 based on a temperature of 80°C. and said polymer being dissolved in about 250 to 400 parts by weight of a hydrocarbon solvent, 1 to 10 parts of an initial tack and bond strength improving resin of the group consisting of wood rosin derivatives, phenol-formaldehyde resins and coumarone-indene resin, and about 30 to 70 parts by weight filler of which at least about 40% is made up of fibers.

Resin-Impregnated Leather Board. U. S. Pat. 2,601,671. L. H. Wilson, Greenwich, C. G. Landes, New Canaan, and C. S. Maxwell, Old Greenwich, Conn., assignors to American Cyanamid Company, New York, N. Y. Appl. Oct. 23, 1946. In a method of making leather board by the steps of preparing an aqueous suspension of fibrous sheet-forming material including a major proportion of leather fibers, impregnating the fibrous material with a water-insoluble hydrophobic organic impregnating agent and forming the impregnated fibrous material into a felted product, the improvement which consists in first adding to the aqueous fiber suspension 1-15% of melamine resin, based on the dry weight of said fibrous material, in the form of a colloidal solution of cationic hydrophilic melamine-formaldehyde resin, then aging the suspension for at least 30 minutes, then adding an aqueous dispersion of the water-insoluble hydrophobic organic impregnating agent in deflocculated condition and flocculating the impregnating agent in the presence of the suspended fibers by the action of the cationic melamine resin, and thereby depositing the impregnating agent uniformly on the fibers along with melamine-formaldehyde resin.

Tanning Agents and a Process of Preparing Them. U. S. Pat. 2,603,613. C. N. J. Thomsen, deceased, late of Frankfort-on-the-Main, Germany, by Gertrud Thomsen, adminis-

tratrix, Kelkheim-Munster in Taunus, Germany, assignor to Farbwerke Hoechst vormals Meister Lucius & Bruning, Frankfort-on-the-Main-Hochst, Germany. Appl. May 13, 1949. The products obtained by sulfonating a mixture of colophony and a naphthol at elevated temperatures, heat reacting a phenol with the product thus obtained and then causing formaldehyde to act at temperatures of about 90-100°C. upon the condensation product thus obtained, said products showing good tanning properties even at high pH values.

Artificial Leather Product from a Butadiene-Acrylonitrile Copolymer, Calcined Clay, and Polyvinyl Chloride Resins, and Process of Producing Same. U. S. Pat. 2,695,247. E. C. Schule, Pottstown, Pa., assignor to The Firestone Tire & Rubber Co., Akron, Ohio. Appl. June 17, 1950. Process which comprises (A) milling, at a temperature below 130°F., a preliminary mix comprising (1) a butadiene-acrylonitrile copolymer containing from 30 to 45% of acrylonitrile and (2) a calcined clay, (B) thereafter milling at from 290 to 340°F. the resultant preliminary mix with (3) a vinyl chloride resin selected from the group consisting of homopolymers of vinyl chloride and copolymers thereof with other unsaturated compounds copolymerizable therewith containing at least 80% of vinyl chloride copolymerized therein, the said ingredients being employed in the following proportions:

	Per cent
Butadiene-acrylonitrile copolymer	10 to 15
Calcined clay	10 to 25
Vinyl chloride resin	60 to 80

the aforesaid percentages being based on the total weight of these three ingredients, which three ingredients constitute at least 65% of all materials employed, and (C) thereafter calendering out the composition into a leather-like sheet.

Undistorted Negative Patterns of Animal Hides. U. S. Pat. 2,607,664. F. R. Nissel, Plainfield, N. J., assignor to Union Carbide and Carbon Corp. Appl. Apr. 13, 1950. In the process of making a negative impression in a matrix blank by means of a pattern material composed of an animal hide, the improvement which comprises impregnating said hide with a heat-hardenable resin capable of imparting rigidity and hardness to said hide, cleaning the surface of said hide of any excess impregnant, hardening said resin by the application of heat thereto to cause said hide to become hard and inflexible, and thereafter impressing said matrix with the resin-hardened hide.

Modification of Keratin. U. S. Pat. 2,615,782. J. W. Haefele, Cincinnati, Ohio, assignor to The Procter & Gamble Co., Ivorydale, Ohio. Appl. Aug. 11, 1950. In the process of treating keratin-containing substance to modify chemical and physical characteristics thereof, wherein the said substance is subjected to the action of a sulfur-containing reducing agent and disulfide linkages of keratin are converted to sulfhydryl groups, the separate step of reacting the previously reduced keratin at a pH from about 4 to about 10.5 with an aqueous solution of at least one organic thiosulfate of the group consisting of alkyl, alkenyl and substituted alkyl and alkenyl thiosulfuric acids and water-soluble salts of same to convert reduced keratin to disulfide containing the organic group of said organic thiosulfate.

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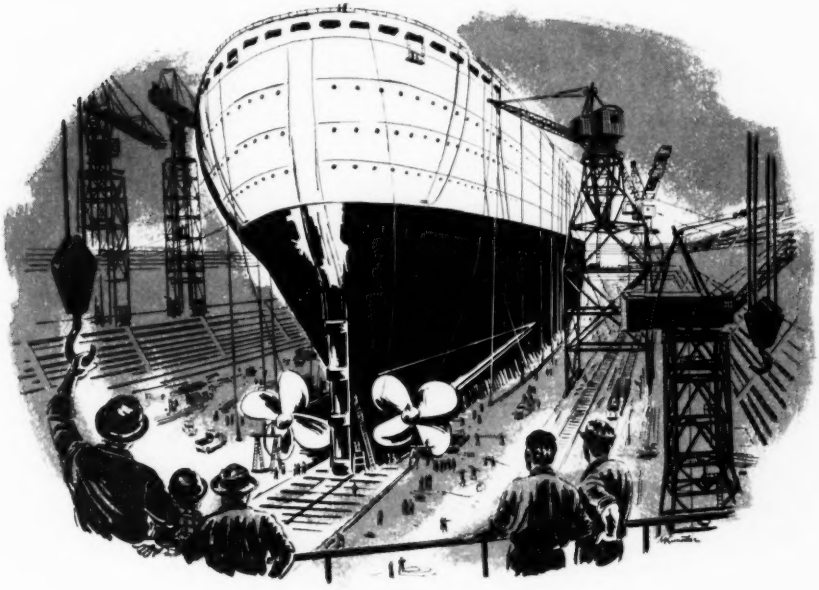

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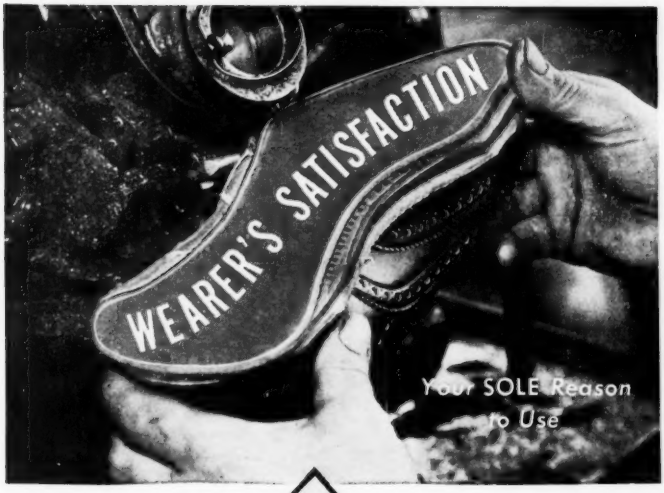

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INDEX TO ADVERTISERS

AMERICAN CYANAMID COMPANY V
AMERICAN DYEWOOD CO. X
AMERICAN EXTRACT CO. ..... Outside Back Cover
APEX CHEMICAL CO., INC. XXIV
ARKANSAS COMPANY, INC. VI
ARMOUR LEATHER CO. XXXV
ARTHUR C. TRASK CO. XXXI
ARTHUR THOMAS CO. XXII
ATLAS REFINERY XVI
BARKEY IMPORTING CO., INC. XXXIV
BARIUM REDUCTION CORPORATION XXV
BONA ALLEN, INC. XXXIII
BORNE, SCRYMSER COMPANY XXXIX
BUCKMAN LABORATORIES, INC. XVII
CALCO CHEMICAL DIV. XIX
CHEMTAN COMPANY XXI
CLINTON FOODS INC. XXXVI
DIAMOND ALKALI CO. XXXI
E. I. DuPONT DeNEMOURS & CO. ..... XXXVII—XL
EISENDRATH TANNING CO. XXVII
FRANK F. MARSHALL XXXI
GARDEN STATE TANNING INC. XXXI
GEIGY COMPANY, INC. XXXVIII
GENERAL DYESTUFF CORPORATION IX
HOOKER ELECTROCHEMICAL CO. XVIII
HOWES LEATHER CO., INC. XXXIII
INTERNATIONAL PRODUCTS CORP. XII
KEPEC CHEMICAL CORPORATION XXXI
LEATHER AND SHOES XXXII
LEATHER MANUFACTURER, THE XXIX
L. H. LINCOLN & SON, INC. VII
MARDEN WILD CORPORATION XXVI
MEAD CORPORATION, THE XIII
NEWARK LEATHER FINISH CO. XXXIII
NOPCO CHEMICAL CO. XXIII
OHIO LEATHER CO., THE XXVII
OLSON SALES AGENCY, THE ..... Inside Front Cover
PACIFIC COAST BORAX CO. XXVIII
PRESTO COLOR CO. XXVIII
REILLY-WHITEMAN-WALTON CO. XXIX
RIVER PLATE CORPORATION, THE XIV
ROBESON PROCESS CO. II
ROHM & HAAS XV
SALEM OIL & GREASE CO. XXX
SAXE CUTCH CORPORATION XXVI
SHOE & LEATHER REPORTER XXX
SOCONY-VACUUM OIL CO. I
SOLVAY PROCESS DIVISION, ALLIED CHEMICAL & DYE CORP. XI
SUN OIL COMPANY XXVI
TANEXCO, INC. ..... XLII—Inside Back Cover
TANIMEX CORPORATION XXXV
TANNERS' COUNCIL RESEARCH LABORATORY XXXVI
TEAS EXTRACT CO. III
UNION STARCH & REFINING CO. XXIV
WALLERSTEIN COMPANY, INC. IV
WARNER CO. XXVII
WHITTEMORE-WRIGHT CO. XXVIII
WOLF, JACQUES & CO. VIII
YOUNG CO., J. S. XX

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MADE FROM LIVE WOOD

TYPICAL A.L.C.A. ANALYSIS

	Solid	Powder	Spray Dried
TANNIN	61.72	66.7	73.5
NON-TANNIN	21.65	21.2	19.1
INSOLUBLES	.65	.6	.7
WATER	15.98	11.5	6.7
ASH	.67	.82	.75

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made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

TANNIN	61.55
NON-TANNIN	16.03
INSOLUBLES	1.70
WATER	20.72

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